Investigation of pollution coming from copper, lead, and zinc mining, and factors controlling mobility and bioavailability of pollutants at Ecton Hill, Staffordshire, UK

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Declaration:

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Abstract

Former mining areas are well-known globally to be a significant anthropogenic source of contaminants being dispersed into the surrounding environment. Various human activities, including ore mineral mining, industrial activities, domestic waste production, and the agricultural application of fertilisers and pesticides, are likely to contribute to the release of huge amounts of potentially toxic metals into the ecosystem, which have harmful effects on the flora and fauna and on human health. Therefore, the main aim of this study is to evaluate the contamination that arises from some selected heavy metals (Cu, Pb, Zn, Mn, Cr, Ni, and V) in topsoil and floodplain samples from the Ecton mining area. Ecton Hill is located in the southern part of the Peak District, Staffordshire, England, and bounded by the River Manifold from the west. This area has been mined for sulphide minerals, which were extracted extensively from the 16th century until the mid-19th century; the area is currently being used for cattle rearing and agricultural purposes. Therefore, it would be worth finding out the extent to which the area has been polluted by the aforementioned metals. To this end, topsoil and floodplain samples were collected and analysed for their total concentrations using XRF technique and different granulometric classes (i.e. clay, silt, and sand) using a (Malvern Mastersizer Long Bed) laser granulometer with a presentation unit of MS-17. In addition, soil specific factors, including organic matter content, organic carbon, pH, Eh, and cation exchange capacity were also measured. Spatial distribution maps were constructed using a GIS approach for the metals studied over the study area.

Contamination and ecological risk assessments were carried out via the geoaccumulation index (I_{geo}) and enrichment factors (EF) respectively. Moreover,

collected soils for different land uses have been assessed using the UK government soil guidelines (i.e. ICRCL and CLEA's SGVs soil values).

Furthermore, the bioavailability, leachability, and fractionation (using five-steps sequential extraction) of the metals in various soil phases were characterised using correlation matrix and principal component analysis (PCA) approaches.

The GIS- based spatial analysis maps reveal that elevated concentrations of the metals are located around the sites of the mining waste in the area.

The contamination assessment results indicate that Cu, Pb, Zn have a contamination degree ranging between strongly contaminated (class 4) and extremely contaminated (class 6).

The results of the ecological assessment by enrichment factor (EF) show that Pb has the highest enrichment factor.

The bioavailability results of the heavy metals under study, via EDTA, show that Cu, Pb, Zn have the highest bioavailable fractions.

The regression analysis demonstrates that Mn gives the best fit regression equation with the highest R^2 value of 0.825.

The leachability results reveal that, of the seven heavy metals, Zn has the highest leachable value, whereas the lowest leachable was recorded for Cr.

Speciation was measured using the five-steps procedure, and the results show that Cu, Pb and Zn are mainly associated with the organic matter fraction, whilst, Cr, Ni and V are associated with the residual fraction.

The principal component analysis (PCA) revealed that oxides of Fe/Al, organic matter, and the clay and silt fractions are the main soil parameters responsible for binding heavy metals to the soil surfaces of the study area.

Changing the redox potential conditions and acidification was investigated and the results indicate that such changes have significant effects on the release of heavy metals from the soil particles at Ecton Hill.

Table of Contents

List of Figures

List of Tables

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Chapter One: Research background

1.1. Introduction

Currently, heavy metal contamination receives a great deal of attention because of its environmental effects. These metals are significant in terms of their accumulation in soils, toxicity, and bioavailability, and they come from a wide range of sources (Wang *et al.*, 2015). The term heavy metal refers to the group of elements in the periodic table that have an atomic density of more than 6 g/cm^3 (Alloway and Ayres, 1993). However, sometimes these metals are also called trace elements because their concentration is less than 100 mg/kg in rocks and sediments of the Earth's crust, unlike other metals such as iron (Davies, 1983). On the other hand, heavy metals can be found with elevated concentrations, especially in mineral ores. Kravtsova *et al*. (2015) reported high amounts of As, Sb, Se, Hg, Pb, and Zn in mineral ores in northern Russia. Furthermore, according to Alloway (1995) some ores have high amounts of some heavy metals and become an economic source of such metals. According to Davies (1980), heavy metals include copper, lead, zinc, mercury, manganese, cadmium, arsenic, iron, chromium, molybdenum, and nickel. In terms of heavy metal sources in the environment, there are two main ones: 1) weathering and erosion of parent materials; and 2) anthropogenic input of heavy metals, including mining processes for extracting minerals, industrial emissions, sewage sludge, agricultural application of fertilizers, motor fumes, and burning of fossil fuels (Nicholson *et al*., 2003, Kachenko and Singh, 2006; Yang *et al*., 2009).

It should be mentioned that under normal environmental conditions, heavy metals are more likely to be introduced into the environment in low concentrations from the weathering of parent rocks (i.e. normal input). These concentrations have been

elevated due to the human activities mentioned above (Kashem and Singh, 1999). In terms of environmental contamination, heavy metals are considered to be the most significant pollutants, with many areas all over the world being found to be polluted by this group of metals due to human activities such as mining, industry, and the extreme use of land for agriculture (Adriano *et al.,* 2004). For instance, in the USA, Pb, Zn, Cr, Cd, Ni, and As are considered to be the major contaminants on lands contaminated by heavy metals and, therefore, they are of special concern (U.S. EPA, 1995). In addition, contamination by heavy metals is not only found in developing countries; it is also seen in advanced countries of Western Europe such as the UK, Germany and France (Marron, 1992; Albering *et al*., 1999; lafray *et al.,* 2014; Chen *et al*., 2016), as well as the USA (Axtaman and luoma, 1991; Rader *et al.,* 1997). Moreover, contamination of soil with heavy metals sometimes becomes too serious and poses an environmental risk to human health and other organisms. Some cases of such contamination have been reported by researchers such as Lacatusu (1996). Furthermore, according to Alloway (1995) the majority of heavy metal contamination cases are likely to be due to improper contamination control at mine sites.

In the UK, according to Gregory (1980), metal mining started since the Roman times and lead was produced in Staffordshire (including our study area). Production reached its highest level in the middle of the 19th century. As a result, huge amounts of mining waste were disposed of in the surrounding ecological environment, and consequently this may have caused heavy metal contamination. Mining waste and tailing are considered to be a significant source of contaminants that can be easily transported via the atmosphere and river waters (Thornton, 1980). In our study area (i.e. Ecton Hill), copper, lead, and zinc were mined for a

long time, resulting in the disposal of huge amounts of mining waste in the environment (e.g. Harris, 1971; Robey and Porter, 1972; Bradley and Cox, 1986; Geeson *et al.,* 1998). As a consequence, the majority of the pollutants accompanying processed ores were transported to adjacent soil and the River Manifold because mining processes in this area comprised many stages, including collecting the mineralized ore, crushing it into small pieces, raw material washing processes using the River Manifold water, and finally, burning the ore to extract the required metals (Barnatt, 2013). Consequently, mining-related pollutants were more likely to be mobilised, causing pollution to the surrounding system, and hence, they pose a risk to human health, animals and plants. To investigate the degree of pollution coming from historical mining in the area and its effects upon the flora and fauna, it is essential to demonstrate the spatial distribution of the potentially toxic metals across the area, as well as their bioavailability and speciation, and the factors that governs the behaviour of heavy metals, such as pH, organic matter, redox potential (Eh), cation exchange capacity (CEC), and soil grain size.

1.2. Thesis structure

In principle, this project will comprise eight chapters. The background to the research, the study area, and the methodology will make up chapters one, two, and three, respectively. This will be followed by the spatial distribution and contamination assessment of the studied heavy metals over the study area (chapter four). Then the bioavailability, speciation of the heavy metals, and factor analysis will be in chapters five, six, and seven respectively. Finally, the conclusions, recommendations for future work and limitations for the research will be in chapter eight.

1.3. GIS- based spatial distribution maps of pollutants

There are many anthropogenic activities that introduce environmental pollution. However, various industrial operations and urban improvement are considered to be the significant drivers for environmental contamination (Tume *et al.,* 2008; Yang *et al*., 2011). As a result, nowadays environmental pollution and its consequences for human health are becoming a key concern for many researchers worldwide. To deal with this problem, techniques are needed, such as the Geographic Information System (GIS). GIS is a computerised data system that has a good ability for displaying, simulating and measuring problems related to environmental components (i.e. soil, air, and water) (Parveen *et al.,* 2012). In addition, this technique enables researchers to find the relationship between pollutants (e.g. rare earth elements and potentially toxic heavy metals) and environmental elements by analysing multilayers of these pollutants with different types of soil (Cheng *et al.,* 2009). According to Walsh (1988), GIS- based maps are very important for studies related to environmental investigations because of their ability to visualise the relationship between different land features and environmental datasets. Therefore, GIS is considered to be a powerful tool for soil contamination research (Meinardi *et al.,* 1995). For example, Zhong *et al*. (2012) have utilised the spatial distribution of heavy metals using GIS to indicate areas of soil polluted with heavy metals (i.e. hotspots, areas of high heavy metal concentration surrounded by areas of relatively low concentration). The GIS technique can help investigators to gain an insight into the present pollution as it gives a map with different colours, which makes it easy to distinguish between polluted and unpolluted areas. In addition, GIS, using geostatistical methods in regard to pollution issues, has enabled researchers to use different spatial interpolation techniques, such as kriging and IDW, which has been

used in the current study. (Briggs *et al*., 2010). Moreover, Bien *et al.* (2004) highlight that spatial distribution and displaying contaminated metals in areas of interest are very important, as they give a better understanding of the source of pollutants, the pathway of exposure and the expected risk. Furthermore, Spatial distribution of potentially toxic metals via the GIS approach has also been used widely in the estuarine environment (e.g. Larrose *et al*., 2010) to evaluate the ecotoxicological influences of trace elements on organisms in the area of interest. Spatial distribution maps and environmental contamination assessment of metals being studied are illustrated in chapter fourth.

1.4. Bioavailability assessment of heavy metals

Generally, the bioavailability of heavy metals can be defined as the amount of metal that can be taken up by organisms (human, animals, and plants) (Adriano *et al.,* 2004). In terms of the forms in which heavy metals might be available in soils and sediments, Li and Shuman, 1996; Sanchez *et al*., 1999; Wong *et al.,* 2002; and Adriano *et al*., 2004, stated that heavy metals might be found in the following forms: soluble and exchangeable fractions (i.e. bound carbonate fraction, and organic bounded fraction). These two forms are considered to be easily and significantly bioavailable, whereas the fractions of Fe/Mn oxides and sulphides are considered to be stationary under normal soil conditions. Compared with the fractions mentioned above, the residual fraction is less bioavailable because this fraction of heavy metals is restricted in the crystal structure of the minerals in which heavy metals are present (Wong *et al*., 2002). It should be noted that different kinds of metals have different levels of bioavailability and uptake by living organisms (refer to table 1.1), and their negative effects on organisms can be indicated using their chemical species more than by their bulk levels in soil and sediments (Alloway,

1995). In addition, heavy metal bioavailability in soils and their uptake by plants tend to be associated with their solubility because highly soluble metals are more mobile and, hence, more bioavailable (Kataba-Pendias and Pendias, 1992; Adriano *et al*., 2004). Furthermore, as mentioned above, different forms of metals display different levels of bioavailability in soils. Many studies have been carried out (i.e. Macklin and Dowsett, 1989; Petruzzelli *et al*., 1989; Ramos *et al.,* 1994; Riise *et al.,* 1994; Asami *et al*., 1995), in which researchers have found that among these metals, cadmium is the most bioavailable element. According to Sanchez *et al*. (1999), cadmium, in mine waste-polluted soil, is more bioavailable than zinc and lead. As a result, cadmium can pose a potential risk to human health when it enters the human body via the soil-plant-human pathway.

Table 1.1: Different species have different bioavailability in soil (source: Kabata-Pendias, 2001).

Metal species	Bioavailability
Simple or complex cations in solution phase	Easy
Exchangeable cations in organic and inorganic complexes	Medium
Chelated cations	Slight
Metal compounds precipitated on soil particles	Available after dissolution
Metals bound or fixed inside organic substances	Available after decomposition
Metals bound or fixed inside mineral particles	Available after weathering and/or

1.5. Distribution of potentially toxic metals across floodplain soils

This River Manifold is significant in the current because it surrounds the area from the western side (refer to chap. 2 for location). Additionally, Manifold River waters were used to wash mineral ore during mining processes (as has been mentioned previously), therefore huge amounts of mining waste was disposed of in the river. As a result, the quality of the floodplain soils of the aforementioned river is likely to

have been affected by the former mining activities mining wastes associated heavy metals. According to Martin (1997), in the fluvial environment, the most well-known contaminants that may be transported are heavy metals. These sediment-related heavy metals are usually accumulated and deposited in areas such as floodplains, river banks, soil bars, and old river channels (Leenaers, 1989a). This is to say, floodplains can be considered as traps for potentially toxic metals, and the storage capacity of floodplains for keeping these metals is controlled by factors such as the association mode between the heavy metals and the floodplain soil, and the stability of the floodplain with regard to the geomorphology of the area (Renwich and Ashley, 1984). In the case of basins, which are unstable geomorphologically, previously deposited sediments can be an additional source of heavy metals in the surrounding environment of fluvial systems whenever they are eroded (Martin, 1997). As a result, heavy metals are becoming the most important group of pollutants in terms of environmental pollution, and are being paid more attention than organic chemical compounds (Adriano *et al*., 2004). Furthermore, Thornton (1980) pointed out that investigation of heavy metals in riverine systems in terms of their movement and storage within fluvial systems first started in the middle of the 1970s.

1.6. Heavy metals: adverse effects and land usage

Since the last two decades, heavy metals are considered to be the most significant environmental pollutants compared to that of the organic ones (Adriano *et al.,* 2014). Currently, various researches have focused on the environmental and human health problems connected to the heavy metals pollution because these pollutants might present in high concentration in soils, which are the main sources of the required nutrients for animal and plant crops (Oliver, 1997). Therefore, heavy

metals can pose adverse effects to human health when consuming plant and animal products.

While many elements in the soil are useful in small quantities, they become toxic when present in greater amounts. For example, selenium (Se) is very beneficial in small amounts for both humans and animals, however, it becomes toxic (poisonous) to brain tissues in high quantities (Oliver, 1997). In addition, the deficiency of metals such as zinc (Zn), which its deficiency is a key problem globally, is linked with many human health problems, for instance, anaemia, skin lesion and delay heal of wounds (Alloway, 1995). Consequently, the adverse effects of heavy metals on human health and other organisms can be characterised using the term “Toxicology”, which deals with the effluences of toxic substances on living organisms and the method by which they transfer into the organisms’ body (Alloway, 1995).

It has been indicated that above a specific concentration, pollutants can have a harm effect on some organisms’ functions, and the concentration at which an adverse health effect take places is called dose-response (Manahan, 1991). In addition, this critical concentration, which also calls threshold value, is different between species and sexes due to the genetic and other factors such as the kind of diet.

According to Rodricks (1992), some toxins can be classified as supertoxins because they have a lethal influence at a small dose of less than 5 mg/kg body weight (see Table 1.2).

Table 1.2: A classification of toxins based on lethal doses for humans (Rodricks, 1992)

Toxicity rating	Probable lethal dose for human (mg/kg body weight)
Particularly non-toxic	>15000
Slightly toxic	5000-15000
Moderately toxic	500-5000
Very toxic	50-500
Extremely toxic	5-50
Supertoxic	<5

In addition, it has been indicated that the toxicity rate for any toxin is controlled by its adsorption, distribution, metabolism and excretion (ADME), and the intense toxic effects are determined by a specific experiment to indicate the dose responsible for death 50% of the total population (LD50) when exposed to the dosage (Rodricks, 1992). Furthermore, it has also been demonstrated that this dose is just an estimated for humans and being indicated using small mammals with so expected errors due to the genotypic differences in vulnerability to a pollutant as revealed in the case of dioxin, which is very toxic compound produced as by-product from various industrial processes, (see table 1.3 for dioxin LD50 for different animals) (Alloway and Ayres, 1997).

The lethal doses (LD50) for some of the metals of the current study are show in Table 1.3.

Table 1.3: Showing the relative mammalian toxicity of metals in injected dose (Bowen, 1979).

Element	Acute lethal doses (LD50) injected into mammals (mg/kg body weight)
Pb	70
Ni	110-220
Mn	18
Cr	90

As a result, in order to reduce the effects of the potential toxic heavy to human health and other organisms, it would be useful to introduce some regulations to control the concentrations of heavy metals in soils as this will help to utilise lands safely for different purposes.

To this end, many countries have prepared guidelines regarding heavy metal concentrations in soils, and the UK government has been in the lead in regard to this matter as will be illustrated in the following section.

1.7. The UK regulations regarding the concentration of heavy metals in soils

Since the concentration of heavy metals in soil may reach a point at which they are more likely to become toxic and cause environmental concerns, it is of great important to legislate rules and regulations to control the concentrations of heavy metals in soils. To this end, many countries have prepared guidelines regarding heavy metal concentrations in soils, and the UK government has been in the lead in regard to this matter. The UK government, namely the interdepartmental committee on the development of contaminated land (ICRCL), published its first guidance in 1983 and then updated it in 1987. In this the concentrations of some contaminants in soils are indicated. This guidance is called Note 59/83 by ICRCL. For many years, the appraisal of the degree of contamination of land was carried out based on this. In 2002, the Department of Environment, Food, and Rural affairs (DEFRA) stated that the guidelines were out of date and needed to be modified in order to be in line with the current laws. Thereby the guidance was stopped and is no longer in use (DEFRA, 2002a). Large areas of land in England and Wales have been contaminated due to metalliferous mining activities (refer to mining history section in chap 2). According to ICRCL (1990) the demand for reclamation of this land has increased, and much of it has been used for stock rearing and pasture for animals.

Thus a new rule was issued in 1990, called Note 70/90. The main purpose of this law was to amend the regulations on contaminated land to eliminate the adverse effects to the environment. In addition, in regard to this law, the term threshold trigger values was used; these are levels of potentially toxic metals in soils, above which the soils are considered to be contaminated to the point that they could harm living organisms, and action must be taken. However, soils with amounts of heavy metals below the threshold trigger values are considered to be uncontaminated and no action is required to be taken (ICRCL, 1990). As mentioned before (refer to mineralization section in chap. 2) Cu, Pb, and Zn are the main elements that were extracted from the study area; these metals are involved in the note above (i.e. 70/90). The threshold trigger amounts for selected elements are shown in table 1.4 (DEFRA, 2002b).

Similarly, in 2002, other countries such as Australia, the Netherlands, and the USA installed similar values for soil (i.e. soil guideline values (SGVs)); soils with amounts above these levels are considered to be contaminated, whereas soils with levels under these values are not polluted and no action required (Table 1.5).

Thereafter, on April 1 2002, a new rule was introduced to deal with contaminated lands in terms of pollution assessment and the remediation of polluted areas.

As stated by DEFRA (2002B), this new act is called “The environment protection Act 1990 (EPA 1990): Part IIA Contaminated land”. According to the Environment Agency (2002b), the main purpose of this law (i.e. Part IIA) is to monitor and eliminate the effects of contaminants that may threaten human health and the environment depending on the mode of land usage. In addition to achieving the

main goal, which is a safe environment, the UK government and the environment protection agency have worked together to update and improve Act IIA.

Table 1.4: Showing guidelines of trigger levels (mg/ kg) in contaminated soil in the UK (adopted from ICRCL, 1990).

Metals	For grazing livestock	For crop growing (Phytotoxicity hazard)	For domestic gardens and allotments	For parks and recreational areas
Cu	500	250	130	130
Pb	1000	-	500	2000
Zn	3000	1000	300	300

Table 1.5: Showing soil guideline values for Pb, Ni, Cr, and Cd for the UK and other countries (mg/kg) (adopted from DEFRA and Environmental agency (2002c, 2002d, 2002e, and 2002f).

Countries and land-use	**Cd**			**Cr**			**Ni**	**Pb**
	pH6	pH7	pH8	Cr (III)	Cr (VI)	Cr Total		
Residential with plant uptake (UK)	1	2	8	-	-	130	50	450
Allotments (UK)								
Residential without plant uptake (UK)	30			-	-	200	75	
Commercial/ industrial (UK)							5000	750
Parks Australia	40			-	200	-	600	600
Residential (Australia)	20			-	100	-	600	300
Commercial/ industrial (Australia)	100			-	500	-	300	1500
Dutch intervention values	12			380	-	-	210	530
Dutch serious risk concentration	13			220	78	-	100	580
USEPA Soil screening level (residential land use)	78			78000*	390* 270**	390* 270**	1600	400

(*) for soil ingestion; (**) for dust inhalation

For instance, the environment protection agency performed a campaign to estimate the number of sites that have been polluted and 33,500 locations were found to be contaminated.

At the same time, the local regime of England and Wales found, at the end of March 2002 that 569 sites have been contaminated with the most common contaminants, metals and organic complexes (EPA, 2002c). Subsequently, a software package called the Contaminated Land Exposure Assessment Model (CLEA) was used to establish the soil guideline values (SGVs). These were used to perform an assessment of the human health risks that come from some of the metals present in contaminated land (DEFRA, 2002b). This software has the ability to appraise the amount of metal taken from contaminated areas by different exposure means. A location specific model was developed (EPA, 2005). Therefore, the soil guideline values derived by ICRCL in Note 59/83 were replaced by those established by the CLEA software. Another important ability of this software is that it can assess chronic hazards to human health from land use pathways, and it can also be used as part of a planning strategy by the local authority (DEFRA, 2002b). In the current study, the Soil Guideline Values established by DEFRA and the Environment Agency, (Tables 1.4 and 1.5) were used to estimate the potential risk that heavy metals can pose to human health for different land uses (chap.4).

It is worth noting that other countries such as Australia, the United States of America, and the Netherlands have also established their own Soil Guideline Values (SGVs) but on the basis of other polices and regulations. In Australia, for example, the Soil Guideline Values for groundwater were established by the national environment protection council in 1999 (NEPC, 1999). In addition, health based levels and ecological based levels, HIL and EILS respectively, were also

established to monitor any expected levels that may cause risks to human health and the ecological system (NEPC, 1999). Another example is the Dutch authority, which has investigated the soil by establishing Invention Values and the Serious Risk Concentration (SRC) for assessment of the degree of soil contamination and to make decisions regarding whether the investigated soil needs remediation or not (Albering *et al*., 1999).

Finally, it should be mentioned that, although it is difficult to make a comparison between soil guideline values for different countries, as different countries have used various policies and criteria to set up their values, such a comparison indicates that the UK values are stronger than others (Table 1.5), as the UK government has used lower values.

In terms of the geochemical fingerprinting, investigate the geochemical fingerprinting of the sediment and soil associated contaminants is very important as it will help to identify the possible source of contaminants under study, and was started increasingly since the end of 1990s, with approaching modern technologies such as remote sensing, new survey technology and photogrammetric being very useful tools for geochemical fingerprinting (Collins and Walling, 2004).

When preforming the geochemical fingerprinting technique, the source areas can be divided geographically into subdivision units depends on the specific factors such as soil types and underlying geology, and each unit representing a specific sediment source, which will then be defined on the basis of the creating process (Weltje, 2012). In addition, this researcher also pointed out that the physical and chemical modification of the source area during weathering process is significant with particle sizes being very important when dealing with these modifications and

assumes that particles with the same sizes, densities and shapes with have similar transportation settings.

Generally, According to Zhang (2012), when achieving geochemical fingerprinting, the general approach includes five key steps; these are characterization of the sediment sources in the catchment, indicate the most effective fingerprinting properties for the specified sources, characterization and collection sediment based on the indicated time frame, using numerical modelling methods to determine the origin of the sediment, and evaluating the validation of the modelling findings.

It is worth noting that, at the study area the geochemical fingerprinting for the source of the fluids that have caused Cu, Pb and Zn mineralization was investigated on the basis of the chemical composition of the fluid inclusions (in pore space) of the rocks of the study area. Consequently, the hypothesis that has been more widely accepted is that suggested by Worley and Ford (1977) for South Pennine Orefields. According to Worley and Ford (1977) the source of the mineralising fluids that have caused lead and zinc mineralisation was the lateral movement of burial formation water.

1.8. An introduction to the heavy metals examined in the current study

1.8.1. Copper

Copper is an element in group 11 of the periodic table. It is the 26th most abundant element in the Earth's crust, and has a mean concentration of 30ppm in the world's soils (Bowen, 1979), and 25ppm in the continental crust (Wedepohl, 1995). Copper has been found with different concentrations in lots of rocks and minerals as a trace element (Wedepohl, 1969). In terms of mineral forms of copper, copper has been found in nature as sulphates, sulphides and carbonates, and as a native metal in reducing conditions (Baker and Senft, 1995). Merian et al. (1991) highlighted that

high concentration of Cu in soils was supplied from the Earth's Crust and this relies on the intensity of weathering, soil formation processes, redox potential, the amount of organic matter in the soil and the pH. Although parent rocks are the main source of copper in soil, anthropogenic inputs of Cu into soil play an important role, including the application of fertilisers, pesticides, mining waste, municipal wastes, paint manufacturing, and food additives. It is well known that the binding and absorption of Cu in the soil is governed by the amount of Fe and Mn, carbonates, and sulphides, whereas concentrations of clay minerals and phosphates have a lesser effect (Jenne, 1968). Regarding the mobility of copper in soil, copper is more mobile under acidic and oxidising conditions, where it has a high mobility within the range of 5 to 6 of PH. (De Vos *et al.,* 2006). In addition, the highest concentration of adsorbed Cu is found in amorphous hydroxides of Fe and Al, clay minerals (e.g. montmorillonite, imogolite, and vermiculite), and oxides of Fe and Mn (hematite, goethite, and birnessite) (Kabata-Pendias and Pendias, 1992). These researchers also mention that the bioavailability of copper to plants depends primarily on the molecular weight of the copper compounds and low molecular copper forms released from degradation of animal and plant remains will increase the bioavailability of copper. Moreover, due to the adsorption and fixation of copper to the soil, copper becomes a less mobile trace element in soils (Baker and Senft, 1995). With regard to the importance of copper for organisms, copper is considered to be very important for almost all biota. For example, plants require low concentrations of about 5-15ppm (Bowen, 1979). The amount of copper in soils probably influences the growth and production of plants. For instance, adding copper to soil to make up for a deficiency of this element will increase plant yield (Baker and Senft, 1995). In terms of copper toxicity to human beings, the risk of

copper toxicity is considered to be low as human beings could tolerate concentration of about 12mg/day as a safer maximum level (WHO, 1996). However, in humans the uptake of 2 mg Cu/day is recommended (Oliver, 1997). In addition, the concentration of Cu above which the toxicity occurs is (250-500 mg/day) (Bell, 1989). Finally, it should be noted that a scarcity of copper in the human body can lead to serious diseases such as anaemia, mental and nervous system impairment and bone problems (Bradl *et al*., 2005).

1.8.2. Lead

Lead belongs to group 14 in the periodic table. It is a chalcophilic element, a high concentration of which is found in silicate-based igneous rocks. The average mean amount of lead in granite rocks is 25 mg/kg and 3 mg/kg in basalt (Bowen, 1979). Lead has a concentration amount of 35 mg/kg in world soils. It occurs in soil in two oxidation states (+2, +4), with the latter being the most dominant inorganic form. In addition, due to its low solubility, this element has a long residence time (Davies, 1995). Lead has the ability to replace K, Ca, Ba, and Sr in minerals from the adsorption sites due to the similarity in their ionic radii. In addition, the most common Pb-containing minerals are galena (PbS), cerussite ($PbCO_3$), and anglesite ($PbSO_4$). Furthermore, mica k-feldspar, plagioclase, zircon, and magnetite are considered to be the most common host minerals that hold trace amounts of lead (Reimann and De Caritat, 1998). In the soil environment, Mn oxides, hydroxides of Fe and Al, organic matter, and clay minerals are potential sorbents for Pb. In addition, Kabata-Pendias and Pendias (1992) stated that different clay minerals have different abilities in terms of absorbing Pb. For example, illite, imogolite and halloysite absorb Pb more readily than kaolinite and montmorillonite. In terms of environmental pollution, the concentration of lead has increased

gradually in our environment, especially in the upper horizon of the soil, as a result of long term usage of this element by humans (over 5,000 years) (Bradl *et al.,* 2005). For instance, lead has been used in a wide range of industries including solder, paints, pesticides, batteries and plastic. All of these industries have contributed to the release of this element into environment (Reimann and Caritat, 1998). In terms of the necessity of this element as a nutrient for flora and fauna, no biological importance is indicated in this context; it has high toxicity especially for the aquatic environment and children (Smith, 1999).

Pb is especially damaging the brain motor function, and particularly in children, with an uptake of more than 500 µg /day is considered to be harmful to health (Fullen and Catt, 2004), with a lethal intake level of 10000 mg/day (Bell, 1998). The bioavailability of this element from inhalation depends mainly on the particle size. A particle size of 0.05µm has been indicated to be responsible for about 34% - 60% of the inhaled lead (Apostoli *et al.,* 2006). Finally, headache, fatigue, vomiting, production of haemoglobin and impairment of kidney function are the common symptoms of lead toxicity (Bradl, 2005).

1.8.3. Zinc

It has been indicated that concentration of zinc in mafic rocks, such as basalt (100 µg/g), is more than that of felsic rocks, such as granite (52 µg/g), and with mean amount of (90 µg/g) in soil materials (Bowen, 1979). Furthermore, the concentration of this element has been found to be higher in shale and clay material (80-120 µg/g) than in sandstone rocks and calcareous rock such as limestone and dolomite (10-30 µg/g) (Kiekens, 1995). Sphalerite (ZnS), smithsonite ($ZnSO_3$), fraklinite ($ZnFe_2O_2$), Zincite (ZnO), and boyleit ($ZnSO_4.4H_2O$) are the most important zinc minerals, and a small amount is found in pyroxene, amphibolite, and

mica (Ure and Berrow, 1982). In soils, zinc comes from both natural sources such as the weathering of zinc containing minerals, and anthropogenic inputs such as the disposal of mining waste. Moreover, the clay minerals iron and magnesium oxides are considered to be the most important constituents that absorb this metal (Wedepohl, 1978). In addition, the pH of the soil medium is the main factor that controls the behaviour of zinc, and in acidic and alkaline conditions, the main factors that govern the adsorption of Zn are cation exchange and organic ligands respectively (Kabata-Pendias and Pendias, 1992). Regarding the importance of zinc to organisms, zinc is considered to be one of the most essential elements because it plays a significant role in the construction and function of hormones and proteins. A lack of this element may cause pancreatic related disease (WHO, 2006). In addition, a deficiency of zinc is believed to cause anaemia, poor wound healing, dermatitis, and nervous system disorders (Mirsal, 2008). In terms of toxicity, zinc is not believed to be toxic to plants, but plants can be toxic to humans and livestock if they are grown on polluted soils (Kiekens, 1995). The recommended daily uptake of Zn is 15-45 µg/day, and the excess uptake (>150 µg/day) is related to health problems such as damage to reproductive system (Fullen and Catt, 2004). However, with respect to the environment, when soils have been polluted with zinc, this can be very serious as this element is related to a group of metals that are too dangerous to the biosphere (Kiekens, 1995). This may be due to wider application of this element, because zinc is considered to be the world's fourth most consumed element after Fe, Al, and Cu (Adriano, 2001; Bradl, 2005). Finally, it should be noticed that the key anthropogenic sources of this metal are the mining and smelting processes of zinc, the burning of fossil fuels (coal and

oil), sewage sludge, and the mining non-ferrous metals, all of which can lead to contamination of zinc (Kiekens, 1995).

1.8.4. Chromium

High concentrations of Cr have been found to be related to mafic and ultramafic igneous rocks, with an average amount of 90 mg/kg and 4 mg/kg in basalt and granite, respectively, and 70 mg/kg in world soils (Bowen, 1979). In terms of key chromium minerals, chromite ($FeCr_2O_4$) and crocoite ($PbCrO_4$) are the most common sources of chromium with possible sources being mica, amphibole, pyroxenes, and spinel (Reimann and De Caritat, 1998). Chromium can be found in many oxidation states, but Cr^{+3} is the most stable form. With regard to mobility, chromium has low mobility under most weathering conditions and its behaviour is similar to that of Fe^{+3} and Al^{+3}. As a result chromium can be found in many oxides as well as in clay (De Vos *et al.,* 2006). It has been found that clay absorption of chromium is governed by pH, and that Cr^{+6} absorption decreases with increasing pH, while Cr^{+3} absorption increases with increasing pH (Kabata-Pendias and Pendias, 1992). In addition, these authors also mention that soils contaminated with Cr^{+6} can be fixed by adding lime, phosphates, and organic matter to the soil, as this will increase the pH of the environment and thereby reduce the toxicity of chromium species. In terms of anthropogenic sources of chromium, chemical catalysts, chrome plating, alloy manufacturing, refractory bricks and pigments are key sources of chromium (Reimann and De Caritat, 1998). Biologically, chromium is very important for the life cycle of many organisms and a lack of this element in animals can lead to many health problems such as diabetes and heart disease (Gauhlhofer and Bianchi, 1991; Langard and Costa, 2007). The recommended beneficial uptake of Cr is (50-200 µg/day), whereas, damaging effects can occur above the level of

400 µg/day (Oliver, 1997). In addition, the lethal intake of Cr is 3000 mg/day (Bell, 1998). Finally, the toxicity of chromium depends on its oxidation state. While, Cr^{+3} is considered to be non-toxic, Cr^{+6} has high toxicity and uptake of it can lead to many health concerns, for example kidney damage, diarrhoea, and bleeding in the ingestion tract, as well as loss of the sense of smell in the case of long periods of exposure to its dust (Gauhlhofer and Bianchi, 1991).

1.8.5. Nickel

Nickel is considered a siderophile element and is associated with chalcophilic and lithophilic phases. It has an elevated concentration in igneous rocks rich in sulphide and ferromagnesian minerals. This element has an average concentration of 0.5 mg/kg and 150 mg/kg in granite and basalt respectively, whereas the world soil concentration of this metal is 50 mg/kg (Bowen, 1979). Furthermore, nickel has been found in high concentrations in soils rich in clay. This element can be found in different oxidation states, however Ni^{+2} is the most stable form at high pH and Eh. In terms of host minerals for this metal, the key minerals containing this element are nickeline NiAs, polydmite Ni_3S_4, gersdorfitte $NiAsS_4$, ullmannite NiSbS, pentlandite $(Fe, Ni)_9S_8$, pyroxene, amphibole, pyrite, garnet and chalcopyrite (Reimann and De Carital, 1998). With regard to mobility, nickel tends to be more mobile under oxidizing and acidic conditions and has a high affinity to precipitating with oxides of Fe and Mn during the weathering process (Kabata-Pendias and pendias, 1992). In addition, Mcgrath (1995) mentioned that in the soil environment, the mobility of nickel increases with a decreasing in both cation exchange capacity (CEC) and pH. In terms of nickel sources, the common anthropogenic sources of nickel are fuel and coal burning, the application of fertilisers, sewage sludge, the petroleum industries, waste disposal, battery production, traffic, and the chemical industry

(Reimann and De Carital, 1998). Nickel is very important to organism's lifecycle as it plays an essential role in their metabolism operations (Bradl *et al.,* 2005; Macrath, 1995). In the environment nickel is a non-toxic element to animals and plants at normal concentrations. However, uptake of the sulphide and oxides of this element can cause respiratory system cancer (Sunderman and Oskarsson, 1991). Finally, it has been documented by WHO (1996) that at high levels, exposure to nickel can cause dermatitis, gastric inflammation and carcinogenic diseases.

1.8.6. Vanadium

According to the Goldschmidt classification of the elements, vanadium belongs to the lithophilic groups with a high concentration in mafic rocks than felsic rocks. Bowen (1979) pointed out that vanadium has an average concentration of 90 mg/kg in world soils and 72 mg/kg and 250 mg/kg in granite and basalt, respectively. However, Kabata-Pendias and Pendias (1992) reported that vanadium has a concentration of 150-460 ppm in soil of mafic rocks origin. The geochemical behaviour of vanadium in the environment is governed by its different oxidation states (+2, +3, +4, and +5) and its ability to substitute with iron, titanium and aluminium in the crystal structure due to the similarity in their ionic radii. With regard to key minerals of this element, carnotite K_2 $(UO_2)_2(VO_4)_2$.3H2O, vanadinite Pb_5 $(VO_4)_3Cl$, and rescolite K (V, Al, Mg) $_2(AlSi_3)$ O10 (OH) $_2$ are the most common minerals for this metal with possible sources being pyroxene, apatite, rutile, sphene, amphibole and mica (Reimann and De Caritat 1998). Regarding the mobility of vanadium, it tends to be highly mobile during the weathering process. It accumulates in residue rocks and is absorbed on the clay surface and Fe oxides, but this mobility can be reduced with the presence of calcium compounds, uranyl cations $(UO_2)^{+2}$, ions of Al, and Fe due to the precipitation of vanadium species

(Edward *et al*., 1995). The anthropogenic sources of vanadium are the combustion of fossil fuel (coal and oil), steel production and traffic pollution (Reimann and De Caritat 1998). Finally, in terms of the biological importance of this element, it is considered to be an essential nutrient to many organisms such as humans, although high concentrations can lead to health problems, including headache, vomiting and weakness, and in some cases it can affect the nervous system causing giddiness and dizziness (Byerrum, 1991, Lagerkvist and Oskarsson, 2007).

1.8.7. Manganese

Manganese is a transition metal that belongs to group seven of the periodic table. It is the 12th most plentiful element in the Earth's crust (O'Neal and Zheng, 2015). It has many oxidation states, including Mn (II), Mn (III), and Mn (IV), with Mn (II) being the most stable oxidation form (De Silva and William, 1991). In the soil environment, it has been found as "nodules" with a black and grey colour coating soil grains, and it is present in an impure form due to contamination with clay minerals and organic matter (Bell, 1998). In addition, the latter author also mentioned that in soil manganese is usually observed to be negatively correlated with the amount of copper and cobalt. With regard to the geochemical behaviour of this element in the soil, according to Erlich (1971), manganese acts similarly to iron and hence has a close distribution mode within a soil profile. It tends to exist in a high valence, such as manganous carbonate and hydroxide, or in a soluble form, such as Mn^{+2}. Moreover, manganese starts to be released in soil solutions at a pH of less than 8 and a redox potential (Eh) of 600 mV. In terms of hosting minerals, manganese can be found as sulphides such as Alabandite (MnS), oxides such as Pyrophnite ($MnTiO_3$), or silicates such as Tephroite (Mn2SiO4) (Nakagawa *et al.,* 2011). With respect to the biological importance of manganese, Thornton (1983)

pointed out that manganese is crucial for many types of birds and animals, in which it presents either as a metalloenzyme, or contributes with other metals in lots of enzyme- metal compositions and affects both the specifications and kinetics of these enzymes. In addition, in mature human beings, Mn has a concentration of 12-20mg with the majority of it being found in the liver, bones and kidneys (Underwood, 1977). The toxicity of manganese to humans is less compared with other metals. However, the normal intake of Mn is ranged from 3 mg/day to 9mg/day (Bell, 1998). Industrial exposure (i.e. steel and batteries production, and coal burning) to this element is considered to be the main source of ingestion via inhalation of the metal dust, which can cause many health problems such as nervous system disorders and lung inflammation; it also increases the mortality average (Gray and Laskey, 1980).

Chapter Two: Study area

2.1. Introduction

The study area (Ecton mining area) is located in the southern part of the Peak District National Park in Staffordshire, England, and bounded by the River Manifold from the west (Fig. 2.1).

The reason behind why Ecton Hill has been chosen as a study area is that, Ecton Hill has a different mineralising condition and sulphide minerals compared to other mining areas of the Peak District Nation Park limestone (White Peak) (Fig. 2.2) such as Castleton, Sheldon and Backwell. From these areas Pb and Zn were the main metals mined with mineralising fluids supposed to be sourced from the east, whereas in the Ecton Hill Cu was the main metal extracted with mineralising fluids seem to be from another source located in the west (marine origin). This has been explained in mineralisation section.

2.2. Geology of the study area

The geology of the area has been described by Harris (1971), who points out that from the Devonian to the Tertiary period, the majority of England and Wales was covered by the following sedimentation units:

1- From the Permian- Triassic period, the lithology was sandstone, the majority of which was red sandstone.

2- In the Carboniferous and Jurassic periods, the common lithology was shales.

3- Finally, a limestone lithology was predominant in the Carboniferous and Jurassic periods.

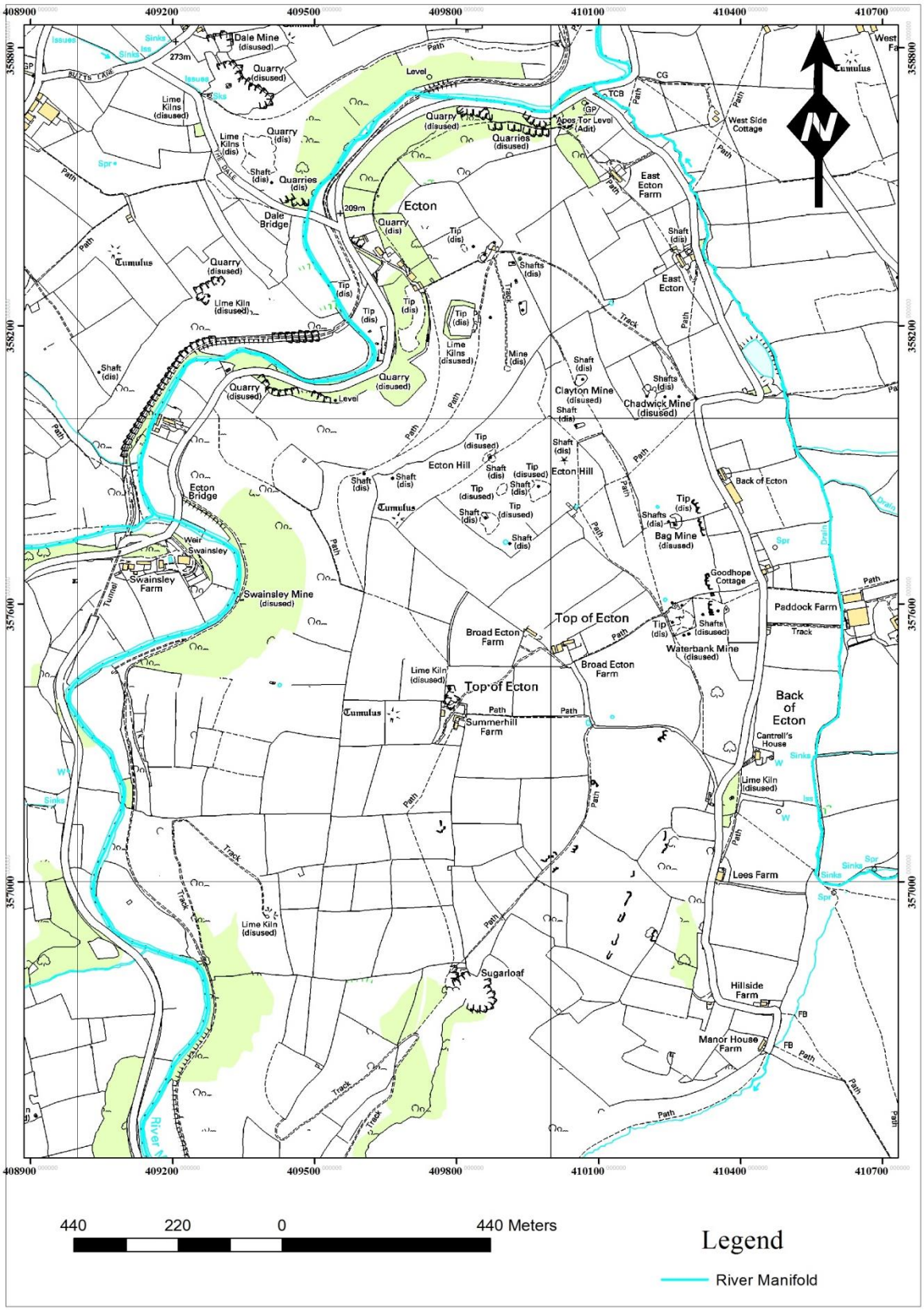


Figure 2.1: Map showing the location of study area (Ecton mining area). Source (modified from Ordinance Survey *et at*., 2009)

In addition, the majority of the Carboniferous Limestone in the study area is located in the south of the Peak District National Park. It has been separated from the Millstone Grit, located in the north of the Peak District, by a soft area of sandstone and shale, which is more likely to be readily weathered to form large valleys such as the River Manifold valley (Fig. 2.3) (Harris, 1971).

Furthermore, the geological outline of the Ecton Hill has been illustrated by Critchley (1979), who shows the stratigraphic succession of the study area by drawing a cross section through the body of the Eton Hill (Fig. 2.4). From this cross section, it can be seen that the Carboniferous Limestone of the study area is covered by the shale beds, which were eroded away until limestone was exposed. It should be noted that the shale outcrops were seen at the eastern side of Ecton Hill during achieving the field work of the current study.

Moreover, Aitkenhead et al. (1985) highlighted that the geology of the study area (Ecton Hill) comprises the following units (Fig. 2.5):

1- Milldale and Hopedale Limestone, which is very fine, poorly bedded to massive and medium grey limestone with inter reef facies that indicates deep water environment.

2- Ecton Limestone, which forms light grey and thinly bedded bioclastic limestones.

3- Mixon Limestone and Shale Formation (Widmerpool Formation). This formation forms dark mudstone, sandstones and limestone, with some pyrite, sphalerite and chalcopyrite are found within the mudstone.

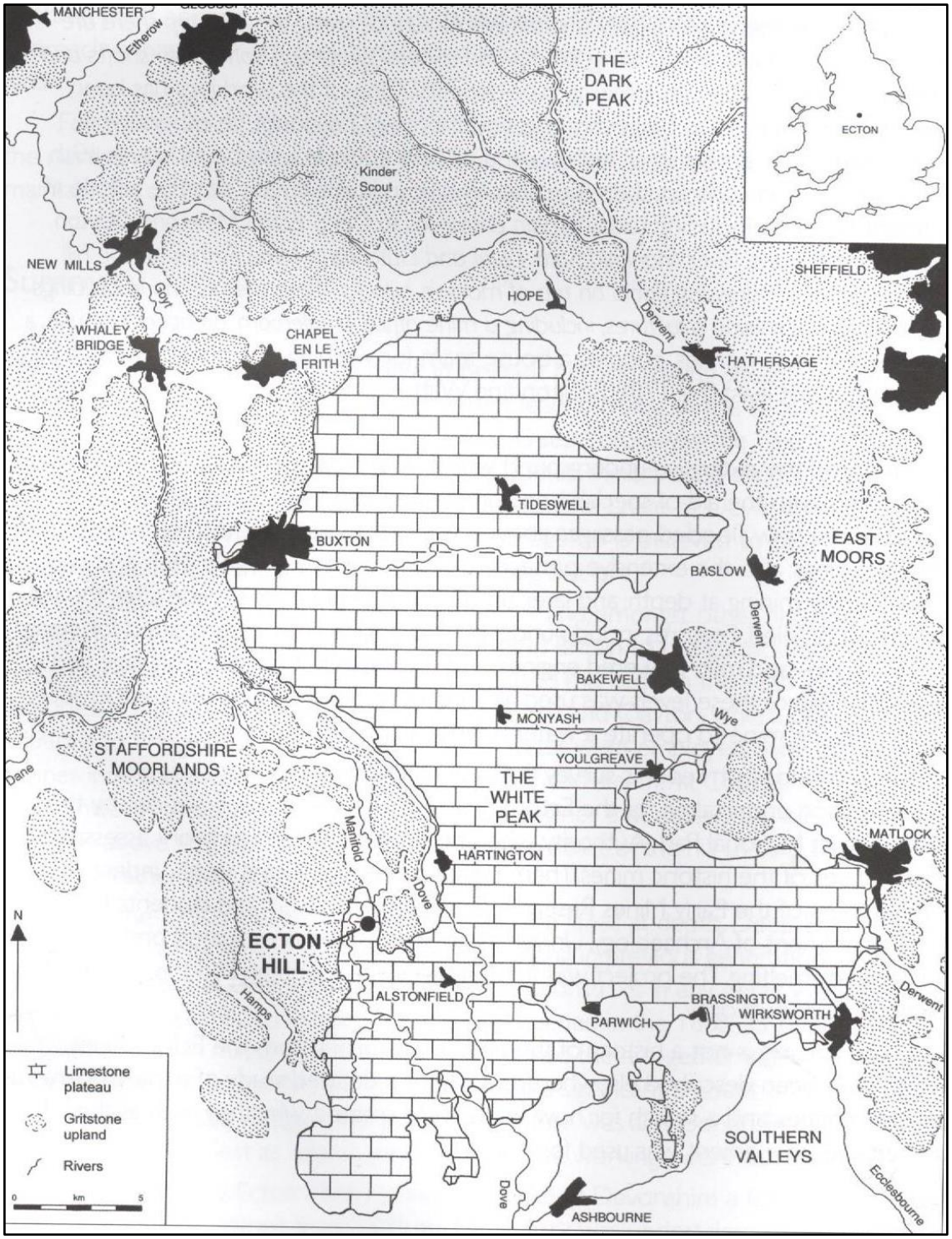


Figure 2.2: Map of Peak District, Showing the study area (Ecton Hill) which covered by Carboniferous Limestone (White Peak) (adapted from Barnatt, 2013)

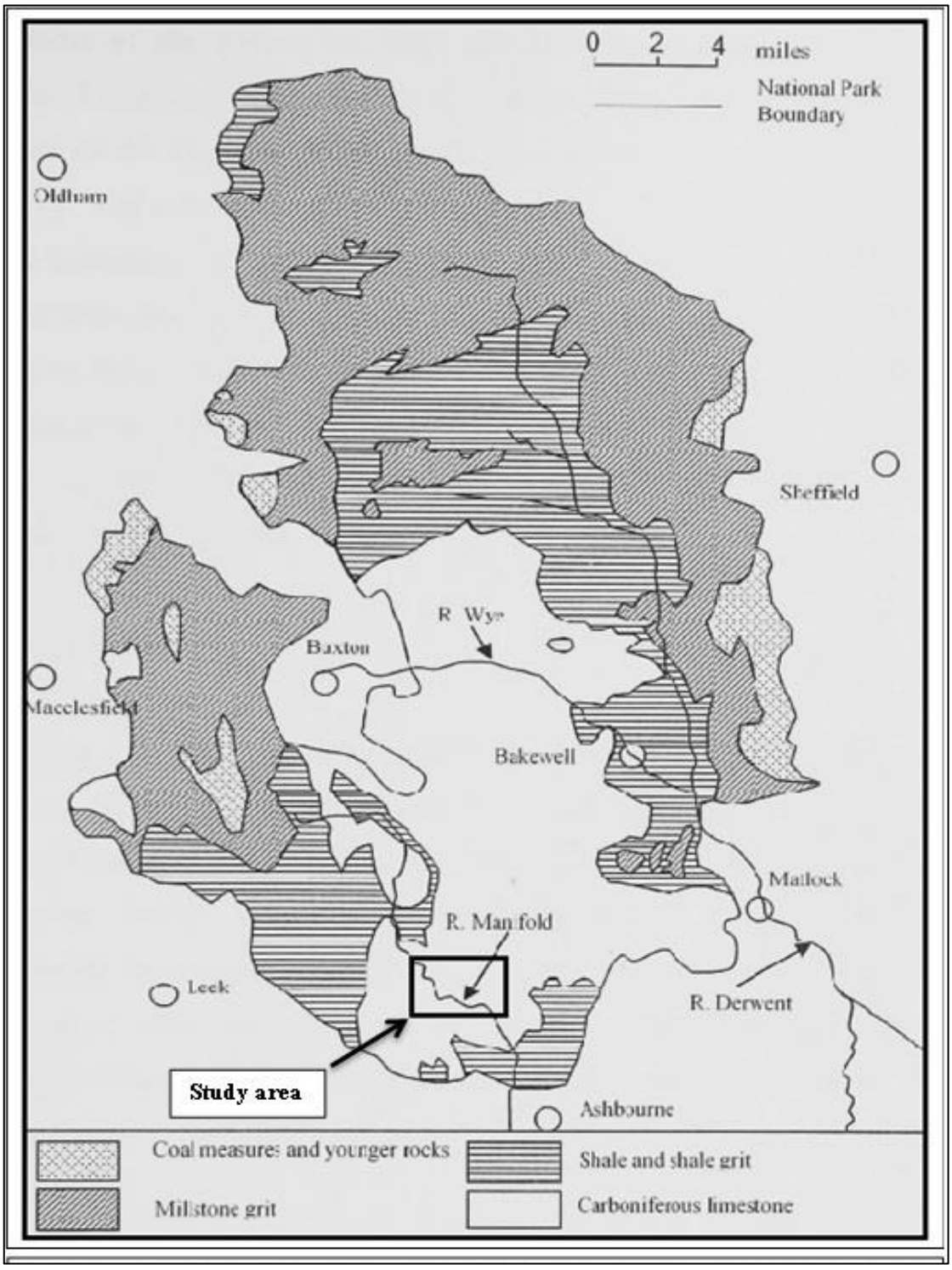


Figure 2.3: Geological map of Peak District showing location of Study area and the River Manifold: Source: modified from (Harris, 1971).

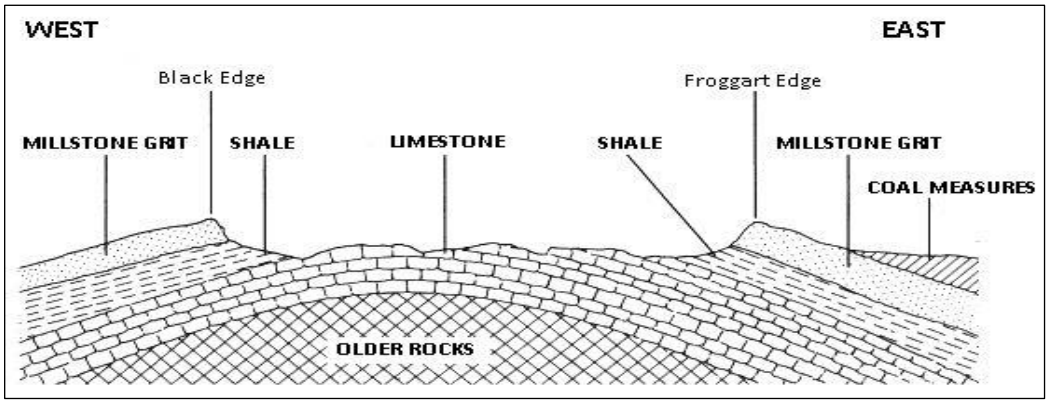


Figure 2.4: A cross section through the study area (Ecton Hill) showing the main geological units (Critchley, 1979)

4- Namurian rocks, which reveals a gradual change from reef limestone to mudstone and sandstone.

5- Mercia Mudstone, which is characterised by red mudstone and slight siltstone and sandstone.

According to Cope (1973), the study area is characterised by bedrocks consisting of Carboniferous Limestone (Dinantian-Lower Carboniferous) (Table 2.1), which affect both the topography and hydrogeology of the area. From the borehole data, it has been estimated that the minimum thickness of the Dinantian rocks is about 600m around Buxton, and about 1000m in the Eyam area (Dunham, 1973).

Most of the structural elements in the area have been attributed to the stresses of the Hercynian Orogeny Earth movements in the Late Palaeozoic, Upper Carboniferous (Stephanian) times, which has a general direction of East-West as compression, then followed by a tension time (top of the Silesian epoch, 299-303my) resulting in the Derbyshire Dome that responsible for most of the outcrop in the area (Aitkenhead, 1985).

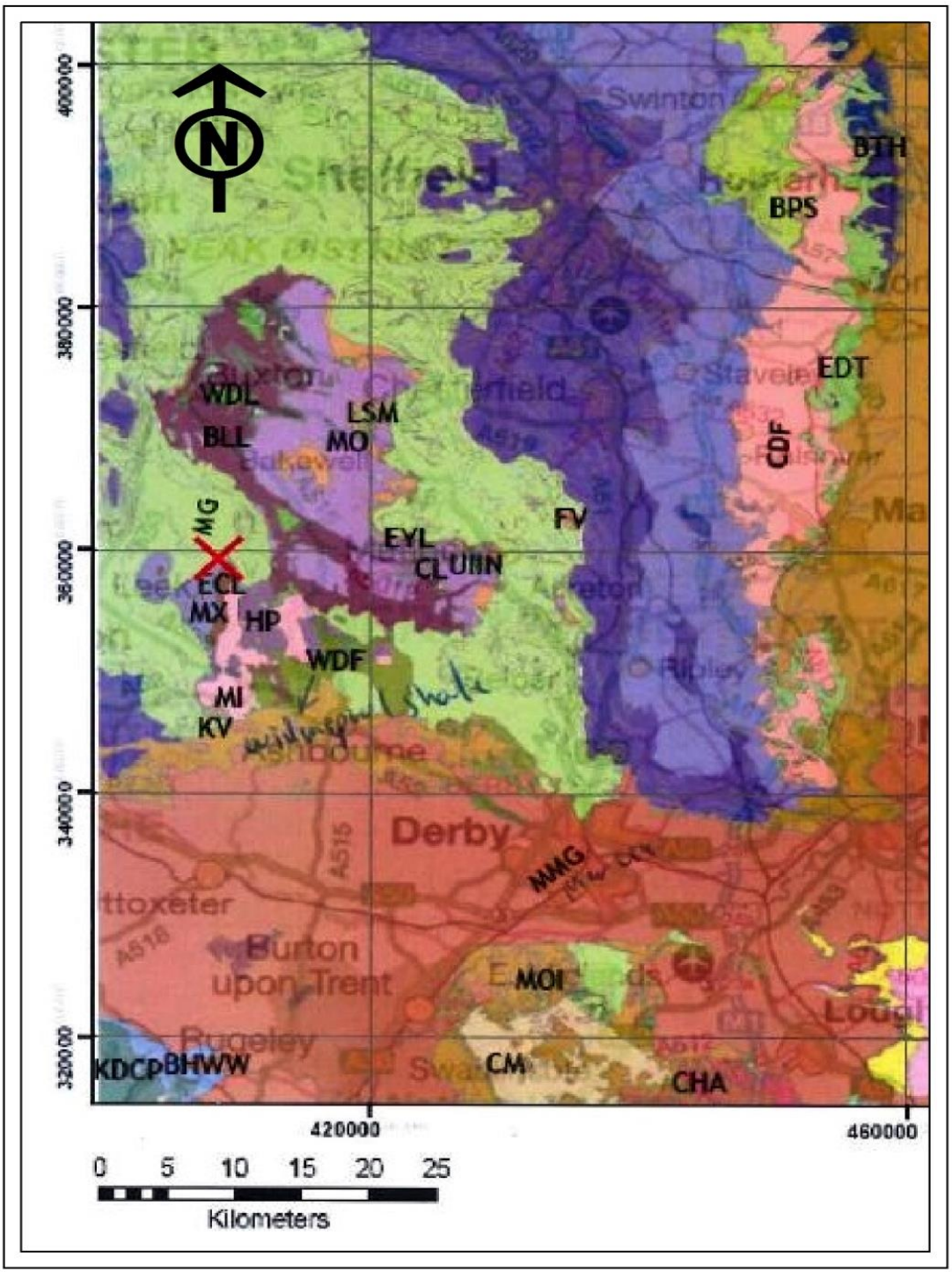


Figure 2.5: Map showing the general geological setting at the study area. Ecton Hill is indicated by red cross. Refer to table 2.1 for keys to geological units. Data from Ordinance Survey et al. (2009).

Table 2.1: Keys to geological formations around Ecton Hill (OS, 2009)

Code	Formation	Group
BHWW	Bromsgrove Sandstone formation, Helsby Sandstone formation, Wildmoor Sandstone formation and Wilmslow Sandstone formation	Sherwood Sandstone Group
BLI	Blue Lias Formation	Lias Group
BPS	Basal Permian Sands Formation	Rotliegendes Group
CDF	Cadeby Formation	Zechstein Group
CM		Coal Measures Group
EDF	Edlington Formation	Zechstein Group
EYL	Eyam Limestone Formation	Peak Limestone Group
HP	Hopedale Limestone formation	Peak Limestone Group
KDCR	Kidderminster Formation and Chester Pebble Beds Formation	Sherwood Sandstone Group
KV	Kevin Limestone Formation	Peak Limestone Group
LSM	Longstone Mudstone Formation	Craven Group
ECL	Ecton Limestone Formation	Peak Limestone Group
WDF	Widmerpool Formation	Craven Group
GM		Millstone Grit Group
MI	Milldale Limestone Formation	Peak Limestone Group
MMG		Mercia Mudstone Group
MO	Monsal Dale Limestone Formation	Peak Limestone Group
MX	Mixon Limestone-Shale Formation	
UIIN	Unnamed Igneous Intrusion of Unknown Age	
WDL	Woo Dale Limestone Formation	Peak Limestone Group

However, Cope (1999) pointed out that the area during the Late Carboniferous- Early Permian period was affected by the Hercynian Orogeny, which caused a lot of folding and faulting all over the White Peak. Faults are one of the most important structural elements in the area. They have been studied in detail by many researchers, for instance Ford (2000), Firman and Lovell (1988) and Quirk (1988). These authors have tried to explain the relationship between faults and the mineralisation.

In terms of stratigraphy, the area is divided into two regions; the shelf region and the off-shelf region, with different geological units (Fig. 2.6). These two regions are

separated by a ridge of apron- reef facies along the southern and western part of the area.

The shelf region is an area of shallow water deposits that form most of the Dinantian formation, whilst the off-shelf region is an area of deep water deposits that cover the southern-western part of White Peak, including the study area (Ecton Hill) and the Mixon area (Aitkenhead et al., 1985).

The rock units at the study area have been described in detail by Aitkenhead and Chisholm (1982), and are shown in (Table 2.2).

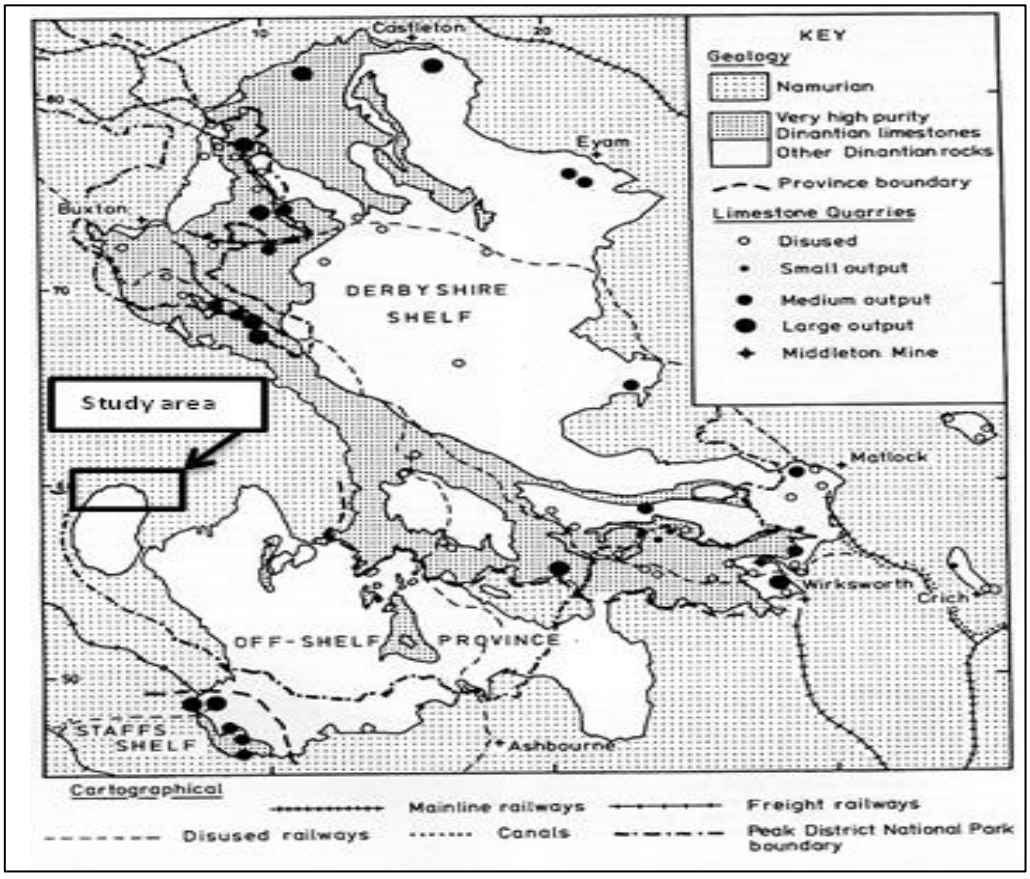


Figure 2.6: Map of study area showing the boundary of both shelf and off-shelf regions (Firman and Lovell, 1988).

Wsetphalian	Mudstone, sandstone, Coal			155 m				
Namurian	Yeodonian to Kinderscoutian		Mudstone, Grits, including Rough Rock, Roaches, Carsworth and Kinderstone grits icluding Rough	840 m				
	Chokierian to Pendleian		Mudstone, Sandstone, Shale	450 m				
Shelf region					Off Shelf region			
Dinantian	Brigantian	Longstone Mudstone Formation	Mudstone	240 m	Brigantian to Asbian	Mixon Limestone-shale Fom. Hopedale limestone Fom.	Limestone, Mudstone, sandstone Reefs	190 m
		Eyam Limestone formation	Limestone reefs, cherty limestone					
		Monsal Limestone formation	Limestone, Lava, tuffs					
	Asbian	Bee Low Limestone formation	Limestone, Lava, tuffs	180 m	Asbian	Ecton Limestone	Thin limestone	200 m
	Holkerian to Chadian	Woo Dale Limestone formation	Limestone, Dolomite	400+ m	Arundian to Courceyan	Milldale Limestone	Thin limestone, lava, tuff, Reef Knolls	800 m
Major Unconformity								
Pre- Carboniferous Basement Locally Devonian, Lower Palaeozoic volcanics and sediments? Charnian rocks								

Table 2.2: Stratigraphic succession of both shelf and off-shelf regions in the north and central Peak District (Aitkenhead et al., 1985)

2.3. Mineralisation

Mineralisation of sulphide minerals had occurred in many locations in the UK with various associated metals, For example, North pennine (Pb, Zn, F, Cd, Ba), Central Wales (Pb, Zn), Lake District (Cu, Pb, Zn, W), Mendips (Pb, Zn, Cd), West Shropshire (Pb, Zn), and South Pennine, which includes current study, has Pb, Zn Cu, F, and Ag associated with (ICRCL, 1990). In the Peak District, where Ecton Mines are located, the most northerly mineralization was happened in the Castleton area and continued south-westwards to Tideswell area (Harris, 1971). In addition, Sheldon, the land around Great Hucklow, east to Stoney Middleton, south of Backwell (Youlgreave and Alport) (Fig. 2.2) are areas had intensive mineralization with mining remains and signs can be found abound (Harris, 1971).

The South Pennine Ore Field mineralisation, includes Ecton Hill, is widely accepted to be classified as a Mississippi Valley Type (MVT) ore deposit, for which Carboniferous Limestone are the host rocks for such mineralisation (Mostaghel, 1985). in addition, Ixer and Vaughan (1993) highlighted that it is generally agreed that the South Pennine Ore field, including the Ecton mines, is an example of Mississippi Valley Type ore deposits and the mineralisation of the metals associated has occurred in the faults and joints in the Dinantian Carboniferous Limestone. Such mineralisation has occurred due to the effects of the Hercynian Orogeny movement, which happened during the Upper Carboniferous period (Aitkenhead *et al.*, 1985). Additionally, Mostaghel (1985) mentioned that the bulk of the mineralisation was happened close to the boundary between Dinantian and Namurian (refer to Table 2.1 for formations boundary). However, Ineson and Ford (1982) highlighted that the mineralisation occurs mainly in the eastern part of the Dinantian formation in-shelf region limestone, while a secondary amount occurred in the western part of the off-shelf province (refer to Fig. 2.6 for both shelf and off-shelf regions). The best example of that is the Ecton area, which was a very important site for Cu production during the 19th century. The most economic part of mineralisation is confined to the upper 300m of the Carboniferous limestone, which is located under the basal of the Namurian shale and above the first horizon of volcanic rocks (Critchley, 1979). The main changes occur in the hosted rocks (Dinantian limestones) before mineralisation are (early, late, and post-diagenetic processes (Ixer, 1979b; Orme and Ford, 1970; Quirk, 1988). Banks et al. (2009) pointed out that mineralisation probably has occurred in several phases, reflecting the state of burial and the availability of mineralising elements. In addition, early mineralisation was associated with the release of magnesium, fluoride and hydrocarbons, whereas barium precipitation

appears to have been restricted to the later phases. However, elements such as Pb, Zn, Ba, and F are thought to be dissolved by fluids from surrounding mud rocks, which might be the Carboniferous shales that bounded the White Peak limestone; these were then deposited in the limestone (Donnelly, 2006).

With respect to the minerals found in the Ecton area, chalcopyrite is considered to be the main ore mineral. However, chalcocite and bronite have also been seen (Robey and Porter, 1972). In addition, galena and sphalerite have been exploited in the area from some mines (Porter and Robey, 2000).

Regarding the source of mineralising fluids, many hypotheses have been suggested to explain the source of these fluids. Aitkenhead et al. (1985) pointed out that the most accepted view is that the mineralising fluids have been derived from the sedimentary formation waters that rich in sulphides because of the reducing condition.

However, Depending on the chemical composition of the fluid inclusions in the Ecton area, Masheder and Rankin (1988) believe that the mineralising fluids may have come from the Cheshire Basin (see Fig. 2.7). However, the hypothesis that has been more widely accepted is that suggested by Worley and Ford (1977) for South Pennine Orefields.

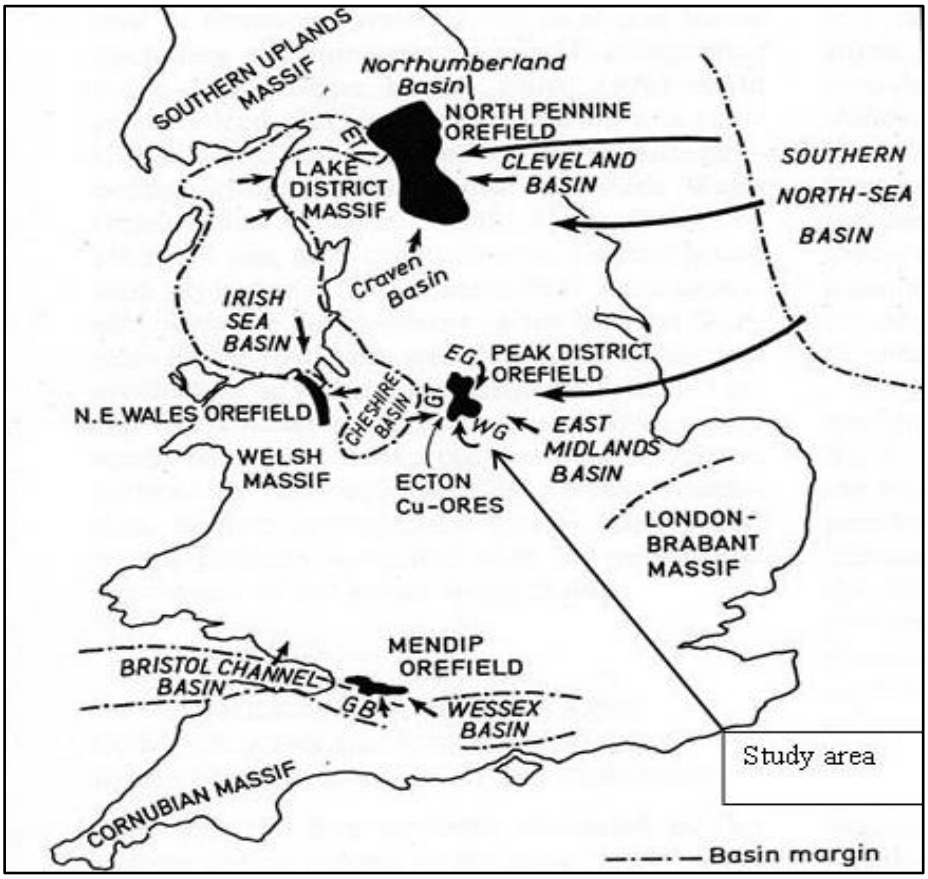


Figure 2.7: Orefield map of Wales and England showing the path direction of mineralizing fluids forming Pb, Zn, Ba, and F mineralization (after Worley and Ford, 1977).

According to Worley and Ford (1977) the source of the mineralising fluids that have caused lead and zinc mineralisation was the lateral movement of burial formation water in the area. However, in the case of Ecton Hill, the mineralizing fluids thought to be from another different source (probably marine) located in the west of the area (Fig. 2.7) and this is strongly supported by the fact that Cu-rich mineralization is only found in this area whereas other areas of the South Pennine Ore field, such as Sheldon and Castleton are characterised by enrichment with lead (e.g. PbS) without the presence of Cu (Mostaghel, 1983).

2.4. Mining history

Harris (1971) states that lead was mined from the Peak District 2000 years ago, since the Rome times, and in the limestone of the Peak District there are many lead-

related evidence can be seen anywhere. However, according to Robey and Porter (1972) the mining history of the area dates back to the Bronze Age.

According to Brearley (1979) mining started in the 17th century, and it is generally agreed that lead was mined extensively by the Romans in the Peak District and that this process continued during the middle ages and up until the early 20th century. In addition, it has been estimated that more than two million tons of lead were extracted from the peak District since the mining first started (Brearley, 1977). However, most of the mines were closed quickly due to problems such as ventilation and flooding (Craddock, 1995)

Regarding the study area (Ecton Hill, SK 100580), on the Carboniferous limestone, which is the main lithology in the area, lead, zinc, and more recently fluorspar have been mined extensively from linear outcrops at the surface known locally as “rakes” (Geeson et al., 1998). It should be noted that in this area copper was the main ore metal mined since the early 18th century under the permission and contracts issued by the land owner, the Duke of Devonshire. The production of Cu is thought to have reached its peak during the period 1776-1817 and more than 66,000 tons of copper ore were extracted (Robey and Porter, 1972). Thereafter, the production was declined as a result of new Cu mines being discovered in Anglesey (Porter and Robey, 2000).

During the period 1830-1850 many mines were worked with a good economic outcome (Brearley, 1977), and by 1880s working was stopped at the Ecton Hill due to reaching water table level and ventilation problems (Robey and Porter, 1972).

By the early 19th century reworking was carried out on the old mining spoils which contain about 6% Cu by washing the metal using the River Manifold water.

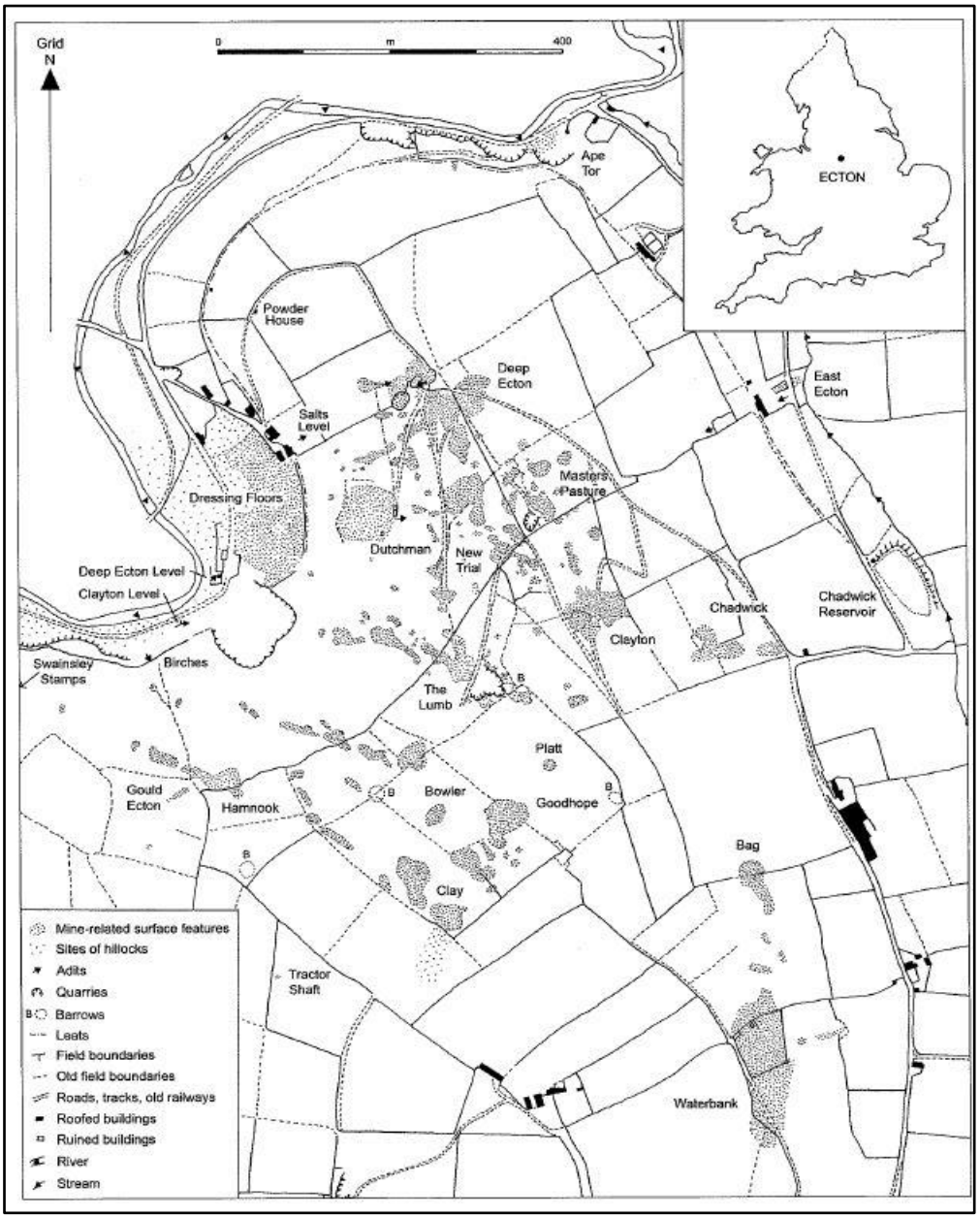


Figure 2.8: Map showing Ecton Hill and its mines (Barnatt, 2013)

Finally, it would be worth mentioning that many mines and smelting locations are still present around Ecton Hill and the main Cu mines were Deep Ecton, Clayton, New Trial, and East Ecton (see Fig. 2.7 for locations), and the periods in which these mines were used to extract Cu from are shown in the table (2.2).

Table 2.3: Showing the main mines at Ecton Hill with working periods (Barnatt, 2013)

Mine	Period
Deep Ecton	1720s-1880s
Clayton	1750s-1880s
New Trial	1850s
East Ecton	1860s-1880s

2.5. Aims and objectives of the current study

Many areas in the UK have been contaminated by heavy metals due to former mining activities. As the study area (Ecton Hill) has been mined for a long period for sulphide minerals (as has been mentioned before), therefore, it is likely that mining wastes and the associated pollutants might have affected the surrounding environment due to the possibility of leaking pollutants from the body of Ecton Hill. Consequently, toxic heavy metals could easily be transferred to an animal's body and, thereby, pose risks to human health and other living organisms in the area.

The aims of this study are to evaluate whether there are high levels of some selected heavy metal (Cu, Pb, Zn, Mn, Cr, Ni, and V) in the topsoil and floodplain samples at the study area (Ecton Hill) and, hence, to determine the possible sources for such elevated levels. In addition, to investigate the degree of heavy metal pollution and how this might influence different land uses. Furthermore, to indicate whether the selected heavy metals are bioavailable and what are the soil specific factors that control fractionation, mobility and bioavailability of metals being studied. Finally to predict a conceptual model to illustrate the role of soil specific factors responsible for binding pollutants to the soil surfaces in the study area.

To achieve these aims, the project will investigate the following objectives:

1- Draw spatial distribution maps for individual elements over the area as this will enable a better understanding of the relationship between mining waste sites and the concentration of toxic metals.

2- Assess heavy metal contamination in the area using the background levels and the UK government guidelines.

3- Identify the bioavailability of the investigated heavy metals and the relationship between the total and bioavailable fractions.

4- Illustrate how heavy metal concentration will be distributed over a cross section of the River Manifold floodplain soils.

5- Characterise the leachability and speciation of metals being studied using leaching test and five steps speciation procedure.

6- Demonstrate the correlation between the concentrations of the investigated heavy metals and organic matter content, soil grain size, and oxides of iron, Mn, and Al using factor analysis (principle component analysis-PCA) and correlation matrix.

7- Finally, construct a model to predict the consequences of changing redox condition and acidification on releasing pollutants from soil particles.

Chapter Three: Research and Design Methodology

3.1. Introduction

This chapter will explain the sample collection, analytical techniques and statistical methods adopted to achieve the present work. The main reason for the soil analysis was to calculate the amount of the constituents, especially heavy metals, which are of great concern nowadays as they have adverse effects when they exceed permissible limits. As a result, the soil sampling and analytical methods used for analysis are very important in terms of the availability to plants of heavy metals and appraising environmental toxicity issues (Alloway, 1995). The precise estimation of potentially harmful heavy metals will help in obtaining a good understanding of their effect on the surrounding flora and fauna. In the current work soil samples, floodplain samples and stream sediment samples were collected and analysed for their total bioavailability, pH, organic matter and chemical species content in terms of selected heavy metals, namely Cu, Pb, Zn, Mn, Cr, Ni and V, in order to investigate the extent to which the area has been polluted with these metals. It has been proven in other studies that areas with a long mining history, for example our study area, have elevated concentrations of potentially toxic heavy metals. The soil sampling and analytical techniques used are described as follows:

3.2. Collecting samples

Prior to sampling, a general tour was made first with supervisors to visit the study area (Ecton Hill). The main reasons for this visit were to explore the area in terms of its stratigraphy and structure, the water resources available, such as rivers, and the location of mining waste and adits, and to collect a couple of topsoil samples for preliminary analysis using a topographic map of 1:50000 (refer to chapter two for study area details).

After that, a plan was made to make a field trip to the study area for one week to collect topsoil and floodplain samples (refer to Fig. 3.1), whose locations were indicated on the map prior to the trip.

Figure 3.1: Study area at the day of sampling

The sampling strategy was to collect topsoil samples randomly, due to the difficulties in accessing all areas as the majority of them are private. However, it was intended to cover the whole study area as much as possible as this will give a better

representing to the area. Soil samples were collected from topsoil (0-15 cm) because it has been indicated that metals are supposed to be more active and mobile within this depth, where there is a large amount of biomass and organic matter, which is very important in heavy metal investigations due to their high ability for cation exchange capacity (CEC) (Adriano et al., 2004). In addition, Bradley and Cox (1990) pointed out that this depth of collection is important because plants absorb the majority of metals from this depth with continual deposition of metals to this depth from river waters. Over a period of six days, 37 and 11 soil samples and floodplain samples, respectively, were collected using a stainless steel spade. Regarding the topsoil samples, to avoid any bias in the collected samples, at each collection point one topsoil sample was collected from a hole with a dimension of about 20cm*20cm*15cm. Then the samples were mixed together in order to achieve homogeneity to represent the taken depth of the site, and the rationale behind choosing this size of hole is to ensure that a standard sampling procedure was followed (Abraham and Steigmajer, 2003, Mcgrath and Loveland, 1992). The collected soil sample locations are shown in Fig. 3.2. With regard to the floodplain soils, as one of the main objects of this study is to identify the pollution effect of mining on the surrounding area, a section across the flood plain, near Ecton Bridge, was taken. From the channel of the River Manifold, a total of 11 samples were collected at an interval of 5 metres. This will help in finding out how the concentrations of the selected heavy metals change from the channel over the floodplain. The procedure for sampling was the same as for the topsoil samples, mentioned above. The locations of the collected section samples (i.e. 11 samples) are shown in Fig. 3.3.

The geographical coordinate systems (Easting and Northing) for all collected samples were recorded (refer to appendices M1 and M2 for samples' Easting and Northing) at the time of sample collection using a Global Positioning System (GPS) tool, as this will help to plot the sample locations when using GIS software to identify the mapping and spatial distribution of the investigated heavy metals over the study area.

Finally, all of the collected samples were stored in polyethylene bags because this helps to eliminate contamination of the samples (Young, 2006). After that, the samples were labelled with the name of the sample, as well as the location, time, and date of sampling using a permanent pen marker. All of the samples were placed in boxes and delivered to the laboratory for processing.

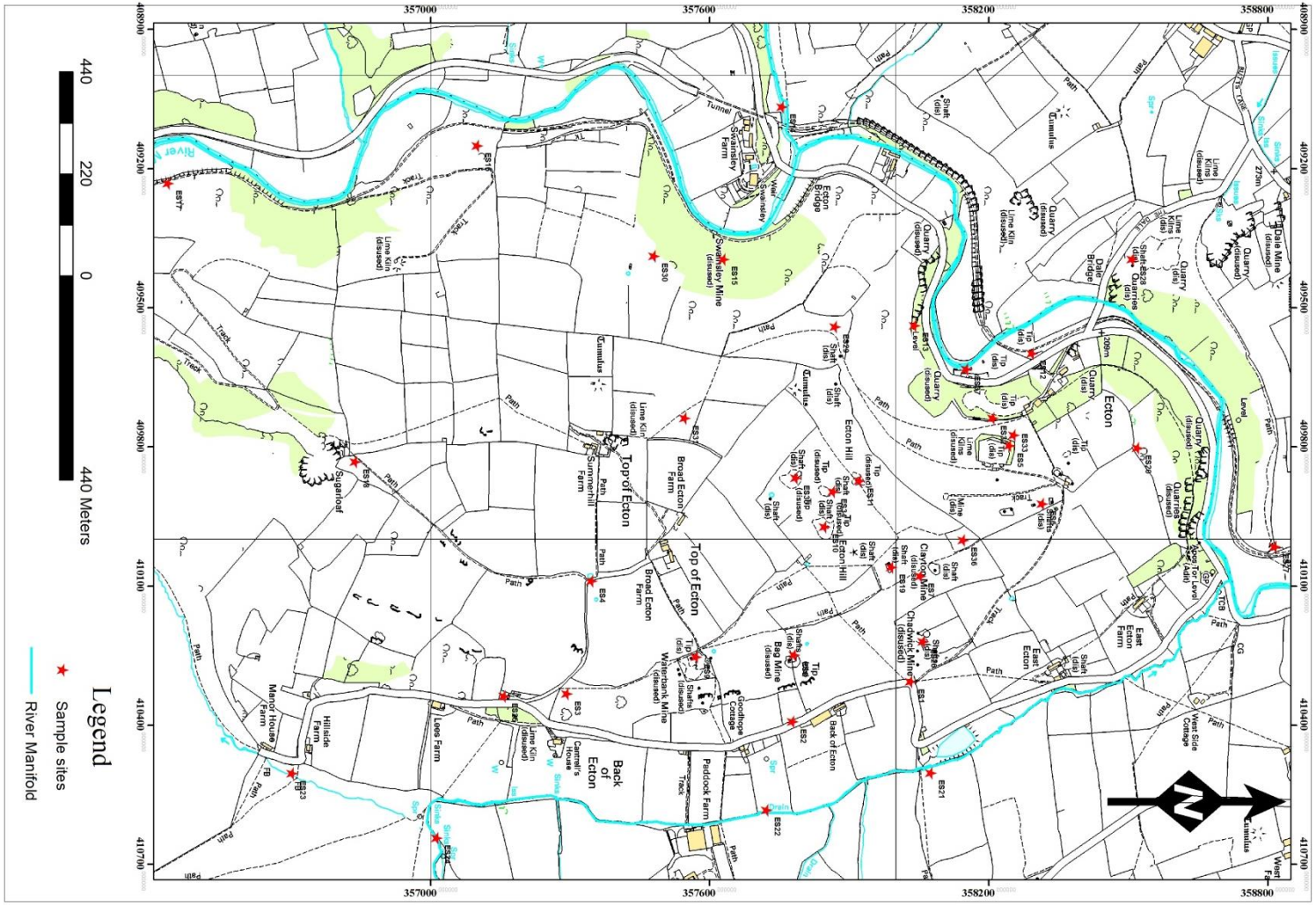


Figure 3.2: Study area map showing location of collected soil and stream sediment samples

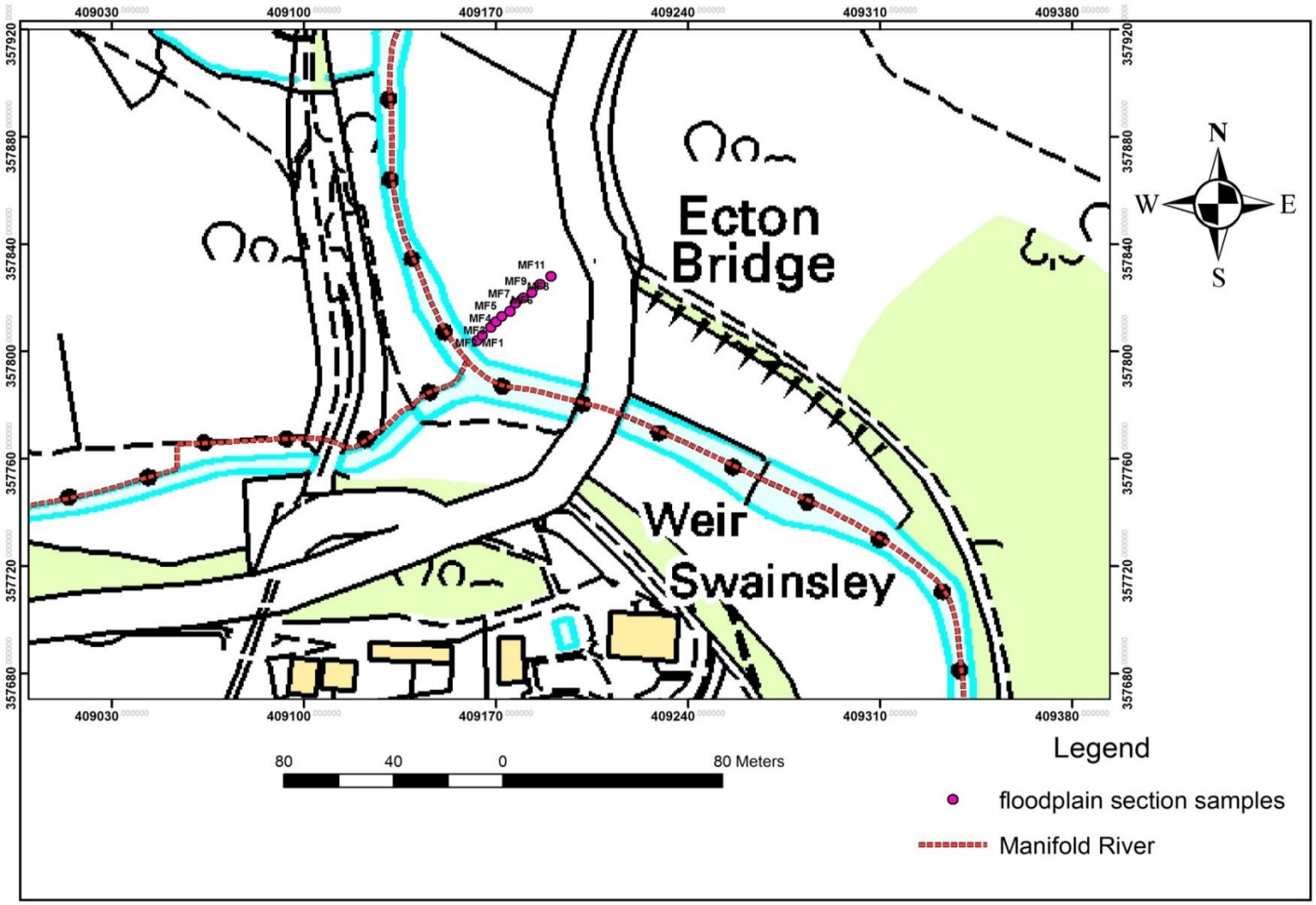


Figure 3.3: Study area map showing the locations of floodplain section samples

3.3. Preparation of samples for analysis

After collection, the samples were transferred to the lab and prepared for analysis. It is worth mentioning that sample processing for analysis is a crucial step as this influences the accuracy of the results obtained. Therefore, sample preparation should be done carefully to minimise contamination as much as possible. For example, Gleyzes et al. (2002) point out that chemical changes are more likely to occur when drying samples and, thereby, cause some errors in the data obtained. Air drying the sample minimises the chemical alteration compared with other drying methods, such as oven drying.

The following procedure was adopted in preparing the samples for analysis, as mentioned by other researchers (Macklin and Dowsett, 1989; Young, 2006).

1- Once the sample bags had been brought to the lab, all of the contents were distributed on a stainless steel tray. This was followed by disaggregation of large pieces and pieces of wood and plant roots were removed. The containers were then labelled clearly.
2- In the lab all of trays were left uncovered and placed at the allocated apace in the cupboard fume, at room temperature, for about seven days as this will help to avoid contamination issues might cause by samples' dust. The samples were turned over and mixed once a day until they were completely dry.
3- Once the samples had dried, they were sieved using a 2mm sieve.
4- Again, large pieces of sample left on the sieve were broken down using a porcelain pestle and mortar and passed through the sieve. After that, all of samples were kept in polyethylene sealable bags with suitable labelling

(i.e. sample name and sieved grain size) in a cupboard until the necessary analysis was to be done.

3.4. Analytical techniques

This section includes a brief description of the analytical methods and instruments used for analysing the samples. Prior to any chemical analysis, all glassware was washed with diluted nitric acid (5%) to get it clean. It was then rinsed with deionised water, and left overnight to dry (Martin, 1997; Zhao, 2001). In addition, it is worth mentioning that all chemical reagents used for analysis were BDH Anala R grade to eliminate the effect of contamination during analysis.

The soil samples were analysed for the total, bioavailable, and chemical speciation of heavy metals, as described below:

3.4.1. X-ray fluorescence (XRF) technique

The collected samples were prepared for analysis using the XRF (Epsilon 3XLE-Model) method to determine the total concentrations of the heavy metals studied. This technique (XRF) is a well-known method for elemental analysis of soils, and has been used, for instance, by the British Geological Survey (BGS) to analyse their soil samples when achieving the geochemical survey project of England and Wales. Results will be used later for both, to draw spatial distribution maps of the studied elements using a Geographical Information System (GIS), and heavy metals contamination assessment. After all of the samples had been dried and passed through a 2mm sieve, as mentioned before, they were then subjected to further grinding using a pestle and mortar and sieved to 125µm. Then 8.5g of the sample powder was mixed with 1.5g wax (Licowax C Microwder) (this helps to bind the particles together when making pellets) and pressed to make pellets for analysis

(refer to Fig. 3.4). After that the prepared pellets were presented to the instrument for analysis. The samples were analysed using the XRF facility at the University of Wolverhampton.

Figure 3.4: Preparation of soil pellets for XRF analysis

3.4.2. Determination of total concentrations (pseudo total) using ICP-OES

The total concentrations of the heavy metals were also determined using the ICP-OES (Agilent Technologies 5100) facility at the University of Wolverhampton. This technique uses liquid system therefore results will be used later when investigating leachability and speciation of heavy metals studied. Although the best way of determining the total concentration of heavy metals is by digesting samples with strong concentrated acids, for instance hydrofluoric acid (HF), and nitric acids, HNO_3/perchloric acid $HClO_4$ (Tessier *et al*., 1979; Tylor, 1996), these acids were ruled out due to safety reasons while working in the lab. Consequently, the samples were digested using a mixture of nitric acid and hydrogen peroxide H_2O_2. Microwave Digester (Milestone Ethos 900 Microwave-Mars 6) was used to digest soils studied. 0.5g of finely ground sample was digested with 5ml of nitric acid and 1ml of

hydrogen (standard procedure designed by the manufacturer for soil samples). The program was set to run at different settings (250W, 400W, and 650W) for about one hour. After digestion, the digester vessels were left to cool down, and then the samples were filtered into a 50ml volumetric flask and made up to 50ml. Finally, the supernatants were transferred into small bottles and labelled to be analysed later by ICP-OES. The results were given in units of ppm. To convert this unit to mg/kg, the following equation was used:

Concentration in (mg/kg) = $\frac{V}{M} \times C$

Where:

V is the volume that the extraction was made up to (i.e. 50ml)

C is the concentration of the element in the filtered solution (supernatant)

M is the mass of sample used (i.e. 0.5 g)

3.4.3. Determination of the bioavailable fraction of the heavy metals

The bioavailable fraction of heavy metals in the soils and sediments was determined. Many researchers have used different methods to simulate the bioavailable fraction of elements in soils, because there is no specific international standard method to achieve this task. However, some researchers, such as Quevauviller (1998), have compared different ways in order to find the best method to give a good simulation for the bioavailable fraction of heavy metals in soils and sediments. This researcher points out that the EDTA (Ethylene Diamine Tetra Acidic Acid) method is a good procedure for estimating bioavailable fractions. In addition, the Ministry of Agriculture, Fisheries, and Food (MAFF) (1986) highlights that the best method for determining the bioavailable fraction of Cu, Pb, Zn, Cd, and Ni is by using (0.05 M EDTA) ammonium salt at a pH of 7 and temperature of 20°C. Furthermore, McGrath and Loveland (1992) point out that as part of the national geochemical survey in

England and Wales for the determination of the bioavailable fraction of Cd, Co, Cu, Pb, Mn, Zn, and Ni, the EDTA extraction method was used. The EDTA extraction method has been used in various studies. In the current study, the MAFF method was adopted to find the bioavailable fractions. The procedure has the following steps:

1- A sample portion of 5g (± 0.01g) was placed into a glass bottle of 250ml capacity
2- A 0.05M EDTA ammonium salt was prepared, and then 100ml of the solution was added to the sample.
3- The bottle (sample and EDTA) was placed on the shaker, and was shaken for one hour.
4- After the shaking process, the mixture in the bottle was filtered using No. 1 filter paper.
5- The EDTA extract solution was kept in small plastic bottles and transferred for analysing using ICP-OES and the results were expressed in units of mg/kg of the dried sample. All samples in the current study were analysed using the ICP-OES facility at the University of Wolverhampton.

3.4.4. Speciation of heavy metals using sequential extraction

In the current study a five-step sequential extraction method was used to determine the presence of different fractions (i.e. exchangeable, bound to carbonate, bound to Fe/Mn oxides, bound organic matter, and residue) of potentially toxic metals in different phases of the soil. Many researchers have used the method of the Community Bureau of Reference (BCR); however, others have used a five-step method. In the present study the different fractions were extracted according the

modified Tessier method, as mentioned by Ure et al. (1993). Based on this method, the extraction procedure for each fraction is described as follows:

1- Exchangeable fraction:

This fraction was extracted by adding 20 ml of magnesium chloride (1 M, at pH7), to each centrifuge tube of 50ml with 0.5g of dried soil sample. The sample was agitated by a rotary spin at 160 r/m for 16 hr, at room temperature.

2- Bound to carbonate fraction:

To the residue of step one, 20 ml of acetic acid (0.11 M) was added, and agitated for 16 hr, as mentioned in step one. The samples were extracted at room temperature.

3- Bound to Fe/Mn oxides fraction:

This fraction was extracted by adding 20 ml of hydroxylamine hydrochloride (0.1 M, at pH 2, acidified using nitric acid HNO_3). Then the sample was agitated for 24hr at room temperature.

4- Bound to organic matter and sulphides:

The residue from step 3 was digested at room temperature with 10ml of hydrogen peroxide H_2O_2 (8.8 M, at pH 2-3) for one hour with some shaking. Then the sample was left in a water bath adjusted to 85°C for one hour. After that, the volume of sample was minimised by some millimetres using a boiling water bath. This step was repeated twice, and then 50ml of ammonium acetate (1 M, at pH 2, acidified by nitric acid) was added to each sample with shaking for 16 hr at room temperature.

5- Residue fraction:

This fraction was extracted by adding a mixture of HNO_3 and $HClO_4$ to the residue from step 4. 5ml of concentrated HNO_3 was added to the sample and heated at 150 °C until approximately dried. Then another 5ml of concentrated HNO_3 and 3ml of H_2O_2 was added to the samples and heated for 3 hours at 150°C. After that, once the samples had been digested, they were left to cool and made up to 25ml.

Finally, at the end of each step, the tubes were centrifuged for a period of 10 minutes, at 4000 r/mins, and the supernatants were separated for analysis by ICP-OES to determine the concentration of the different geochemical fractions in the studied samples.

3.4.5. Total organic carbon determination (TOC)

The organic carbon content for all of the collected samples was calculated using the procedure mentioned by Radojevic and Bashkin (2006). According to this procedure, the soil content of organic carbon can be determined via a back titration with potassium dichromate, which is added to the samples together with concentrated H_2SO_4 in the following steps:

1- 0.5 g of air-dried soil sample was weighed into a 500 ml conical refluxing flask.

2- Then, 10 ml of the standard $K_2Cr_2O_7$ solution was added to the flask and mixed well.

3- 15 ml of the concentrated H_2SO_4 was added a few drops a time until heat was generated and it was swirled carefully to mix.

4- The flask condenser was linked and the water was turned on.

5- The flask was placed on a heat plate, and refluxed for 1 hour.

6- After that, the flask was left to cool, and disconnected from the condenser. About 100 ml of water was added and it was swirled to mix.

7- 5 drops of the chemical indicator (i.e. ferroin –indicator) solution were added.

8- Finally, the mixture was titrated with ferrous ammonium sulphate until the end point of titration was reached, which is when the colour changes from blue-green to violet red.

9- Likewise, all of the steps above were done for a blank sample with the entire chemical reagent used but without the soil samples.

10- The organic carbon content can be calculated using the following equation:

Organic carbon (mg/g) = $\frac{18 \times c \times V \times (1 - V1/V2)}{M}$

Where:

C= the concentration in mol/L of the dichromate solution (0.083 M).

V= the volume of the dichromate solution used in the experiment (10ml).

V1= the volume of the titrant used up (ml).

V2= the volume of the titrant used up in the case of the blank (ml).

M= the weight of the soil sample used (g).

3.4.6. Determination of Cation Exchange Capacity (CEC)

Cation Exchange Capacity for the collected samples was measured using the method described in Radojevic and Bashkin (2006). According to these authors, CEC is the summation of major cations and can be calculated as follows:

CEC = ∑exchangeable cations (Ca^{+2}, Mg^{+2}, Na^{+1} and K^{+1}) in unit meq $100g^{-1}$ soil

The procedure has the following steps:

1- A sample portion of (5g) was placed into a 100ml polyethylene bottle.

2- 25 ml of ammonium acetate solution was added to the sample, and shacked for one hour.

3- After filtration, supernatant was transferred into a 100ml volumetric flask

4- After that, 20ml of ethanol (95%) was added to the bottle, and shacked for one hour, then filtered to the same bottle.

5- This washing process was repeated twice more (i.e. three times).

6- Finally, the extract was made up to the mark (100ml) using deionised water, and analysed by ICP-OES for concentrations of the exchangeable cations mentioned above, then converted to the unit of meq per 100 soils. Results are shown in appendices (M1, M2 and M3).

3.4.7. Grain size distribution

As particle size plays a significant role in absorbing heavy metals, especially clay size due to the high surface area of this fraction, the grain size distribution of the collected samples was determined using a Malvern Mastersizer (Mastersizer 3000, Malvern) Long Bed laser granulomere with an automated sample presentation unit of MS-17 (refer to Fig. 3.5). This instrument uses liquid system, suspension in water.

To prepare the samples for analysis, organic matter should first be removed from the samples, as a high concentration may lead to skewing of the obtained results during the analysis.

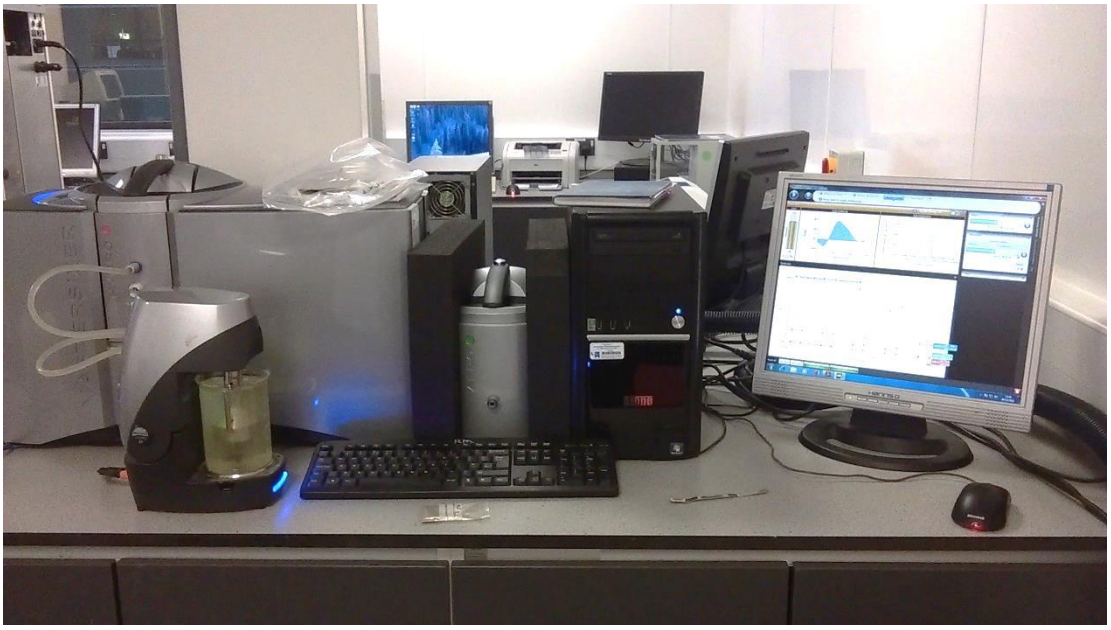


Figure 3.5: Showing Malvern Mastersizer instrument

Therefore, this component was removed using the procedure of Gale and Hoare (1991). According to this method, 50ml of soil sample was placed into a 250ml glass beaker and wetted with some deionised water. A small amount of Hydrogen Peroxide H_2O_2 was added to the sample until the reaction subsided. Then the beaker was placed into a water bath at 70°C and another amount of hydrogen peroxide was added to the sample until no further reaction occurred.

Sample analysis was carried out by, first, adding some drops of sodium hexametaphosphate to each sample as a dispersal agent. Then, a small portion of the sample equal to a small finger nail was taken, after the particles larger than 2mm had removed as these particles had passed the 2mm mesh due to the lack of sphericity. After that, sample was presented to the instrument by washing it off the

petri dish using a pipette. Each sample was analysed in triplicate, and results are presented on the percentage basis for each size. Results are shown in (appendix O). The analysis was carried out using the University of Wolverhampton facility.

3.4.8. Determination of organic matter content

The organic matter for all of the samples collected was quantified. This is very important, as it gives good information about the potential sink of heavy metals in soils. In the current study, the loss of ignition (LOI) method was used to evaluate the amount of this constituent in the studied samples. Many researchers have used different temperatures and different times for ignition. For instance, the organic content was calculated by Martin (1997) using an ignition temperature of 430°C for a period of 24 hrs. However, others, like Giuasti (2001), have evaluated the amount of organic matter using a temperature and period of ignition of 475°C and 2hrs respectively. There is consent that the temperature range of 100-500°C is the range in which organic matter is lost. For example, Bradley and Cox (1986) pointed out that organic matter is liable for weight loss from 100-500°C, while carbonate burning is responsible for weight loss from 500-800°C. In the current study, the method of Giusti (2001) was used to quantify the amount of organic matter. The procedure for this method is as follows:

2 g air dried soil sample (<2mm) was placed in an oven at 105°C for nearly 2 hrs to get rid of the surface moisture. Then the sample weight was recorded (W1). After that the samples were placed in crucibles to burn in a muffle furnace at a temperature of 475 °C for 2 hrs. After ignition, the samples were left to cool, and the second weight (W2) was then recorded. Finally, the following equation was used to find the percentage of organic matter for each sample:

$$\text{OM (\%)} = \frac{W1-W2}{W1} \times 100$$

Where:

W1 is the weight of sample at 105°C (before ignition)

W2 is the weight of sample at 475°C (after ignition).

3.4.9. Measurement of sample pH

The pH is crucial in environmental studies, especially when studying environmental pollution caused by potential toxic metals (refer to pH section), because in many scenarios pH controls the mobility and bioavailability of the heavy metals. To this end, different people have used different methods to indicate pH. Some researchers, such as Pichtel and Salt (1998), have measured pH using a ratio of 1:2 (w/v) soil/deionised water. However, others have used a ratio of 1:2.5 soil/ water, for instance, Narwal and Singh (1998). In addition, the pH of soil has been measured by other researchers, for example Bradley and Cox (1986), using distilled water and a solution of $CaCl_2$ (0.01M $CaCl_2$) in a 1:3 soil to water ratio. It should be mentioned that some investigators, such as Troeh and Thompson (1993), highlight that the amount of water utilised should be indicated carefully, as a high pH reading can be recorded when a high ratio of water is used. In the current study, Narwal and Singh's (1998) method was adopted to determine the pH of the collected samples. According to this method, a 1:2.5 soil/ deionised water ratio was used. 5 g of each sample, air dried (<2mm fraction), was placed in a 50 ml centrifuge tube, and 12.5 ml of deionised water was added. After that, the mixture was shaken for 30 mins and left overnight to settle (refer to Fig. 3.6). The pH meter was calibrated using two calibrated solutions (i.e. pH 4 and 7) prior to measuring. Then the pH meter was used to measure the pH for each sample by placing the electrode head in the

mixture while moving the supernatant until the reading of the meter was stable. All of the readings were taken twice for checking purposes. Between each two samples the electrode was rinsed properly with deionised water to make sure the reading was correct.

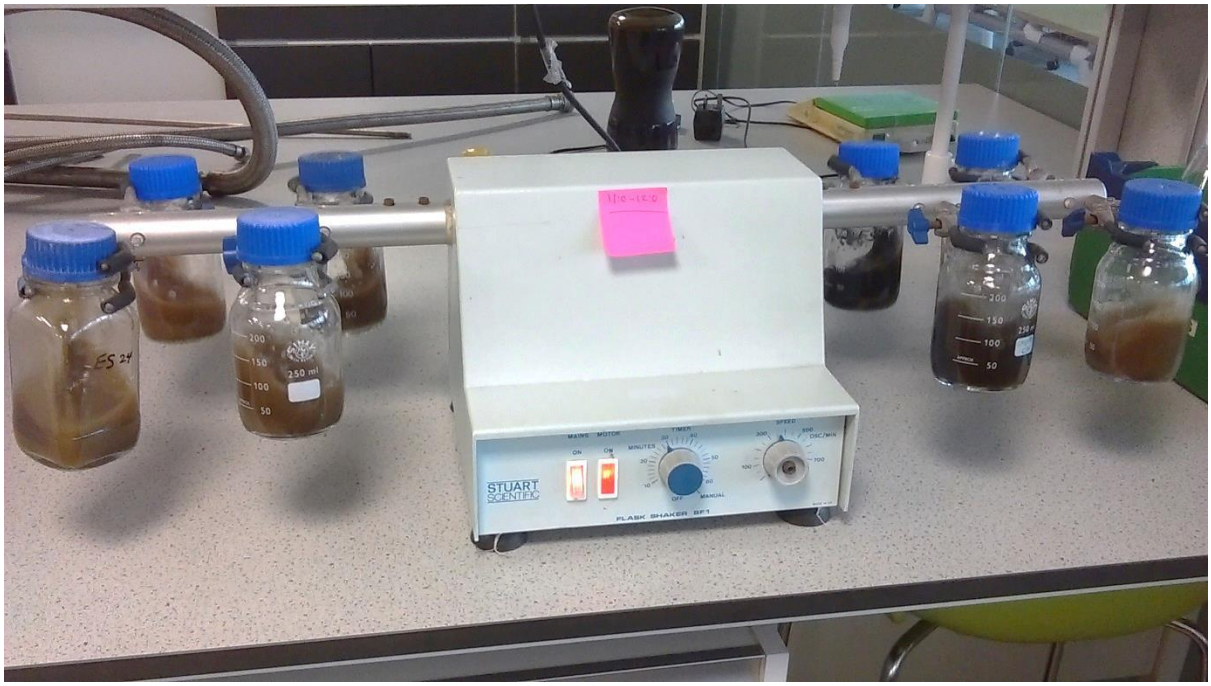


Figure 3.6: Shaking process for measuring soil pH

3.4.10. GIS analysis

Multivariate analysis was carried out using Arc GIS software package (Arc GIS 10.1 version) so that the spatial variation of the metals studied above the study area can be illustrated. This software, as has been mentioned previously- see section x in chap.1), is a computerised data system that has a good ability for displaying, simulating and measuring problems related to environmental components (i.e. soil, air, and water) (Parveen et al., 2012). To this end, GIS- based spatial distribution maps have been drawn using the following steps:

1- Using the Global Positioning System (GPS) instrument, the geographical coordinates (Easting and Northing) for all the collected samples were recorded at the time of sampling (refer to Fig. 3.7).

Figure 3.7: Showing Global Positioning System (GPS) instrument for recording the geographical coordinates for collected samples

2- In the office, all the related dataset (e.g. sample number, sample ID, Easting, Northing, and metal concentrations) have been tabulated in an excel work sheet.

3- Once the Arc GIS has been run, the excel work sheet has been imported and the spatial distribution maps have been illustrated as follows:

   From system toolboxes > spatial analyst > interpolation > finally choose Inverse Distance Weighted (IDW) followed by enter.

4- After the maps have been drawn, all other maps' elements such as legend, scale and north arrow have been added to the map from the insert menu.

5- Finally, from the file menu, the drawn map has to be saved as a picture (JPG) or PDF format to use it latter for the intended purpose.

3.5. Statistical analysis

Once all of the analysis methods previously mentioned had been carried out (i.e. total heavy metals, bioavailable fraction, different geochemical fractions from sequential extraction, leaching test fractions, pH amount, and organic matter content), descriptive statistics (i.e. mean, maximum, minimum, standard deviation) of the obtained results were found using SPSS software package version 20. In addition, the SPSS software was also used to investigate the relationships between different variables, including different particle size fractions, the studied heavy metals, pH and organic amounts, using principle component analysis (PCA), which is considered as a reliable method to find how different variables are associated together. This method has been used by many other researchers, such as Pang et al. (2015), Xiaoling *et al.* (2016) and Maiz *et al.* (2000). Moreover, Microsoft Excel 10 was also used in the present work to work out the degree of contamination (refer to contamination assessment section). Finally, this software was also used to evaluate how the metal concentrations changed from the River Manifold channel within the floodplain section using regression analysis, which was used to find the best equation to explain the association between the metals studied and the distance.

Chapter Four: GIS-based spatial distribution maps and contamination assessment of selected heavy metals in the study area

4.1. Introduction

In this chapter the spatial distribution maps and contamination evaluation of the studied metals in the collected topsoils over the study area have been illustrated. It should be noted that the values of metals studied in the limestone (Table 4.2) have been taken as a background levels to reflect the local geology. Results of analysis are illustrated bellow:

4.2. Geochemical maps for the metals being studied using GIS mapping

In this section, the spatial differences in the concentrations of the selected heavy metals (i.e. Cu, Pb, Zn, Mn, Ni, Cr, and V) over the study area are investigated using the inverse distance weighted (IDW) method of the Geographic Information System (GIS). This approach has been considered to be an efficient way to display contaminant amounts spatially in environmental pollution studies and has been used by many researchers (e.g. Liu et al., 2006; Zhong et al., 2012; Shao et al., 2014; Wang et al., 2014; Hoehun et al., 2014;) (See section 1.2). The spatial distribution maps for each element mentioned above are illustrated below as this may help to distinguish contaminated areas with heavy metal sourced from anthropogenic activities such as mining and the agricultural application of fertilisers.

4.2.1. Copper

The mean concentration and spatial distribution of copper in topsoil samples over the study area are shown in table 4.1 and figure 4.1 respectively. It can be seen that the Cu content in the studied soil samples ranged from 11.8 mg/kg to 5126 mg/kg (Table 4.1).

Table 4.1: Showing descriptive statistics of total heavy metal concentration (mg/kg) at study area

Statistical variables	Cu	Pb	Zn	Mn	Cr	Ni	V
Mean	593.9	3176.9	2314.7	1074.5	35.8	38.3	39.3
Max	5126.0	36644.3	14378.3	3478.8	99.0	134.8	114.0
Min	11.8	28.8	68.0	127.5	1.0	11.3	0.5
SD	1326.8	7306.0	3601.7	812.6	20.9	24.0	25.9

Depending on the concentrations of the studied heavy metals in the limestone as a background (Table 4.2), it can be seen that the Cu concentration in most of the study area was above the limits of the limestone (i.e. 15 mg/kg) especially in the samples from the northern part of the area (Fig. 4.1, dark brown colour). The reason for such elevated concentrations is most likely to be due to the proximity of these samples to the location of mining waste (Fig. 4.2, red circle), where Cu was extracted. In addition, as the area has a long mining history (refer to mining history section in chap. 2) and ore metals were extracted from the area, the mining waste produced has left high concentrations of contaminant metals and this seems to be attributed to poor ore separation during the extraction process as has been highlighted by Alloway (1995). Furthermore, the majority of the mining areas in Britain during the time of mining operations were not controlled by specific laws regarding, for instance, how to discharge industrial effluents or mining waste (Davies, 1983). This might be another reason why high amounts of Cu were recorded at the study area and especially in those soil samples (e.g. ES5, ES6, ES12, ES32 and ES 37) around old Cu mines. This has been confirmed by ICRCL (1990), who highlighted that high concentrations of heavy metals in soils around mining areas were recorded in many areas in the UK. Therefore, it can be concluded that such elevated concentrations of Cu are most likely to be anthropogenic inputs due to the former mining operations in the area.

Table 4.2: Heavy metal abundance in the limestone (background) (adopted from Levinson, 1974)

Metals	Cu	Pb	Zn	Mn	Cr	Ni	V
Concentration limits mg/kg	15	8	25	1100	10	12	20

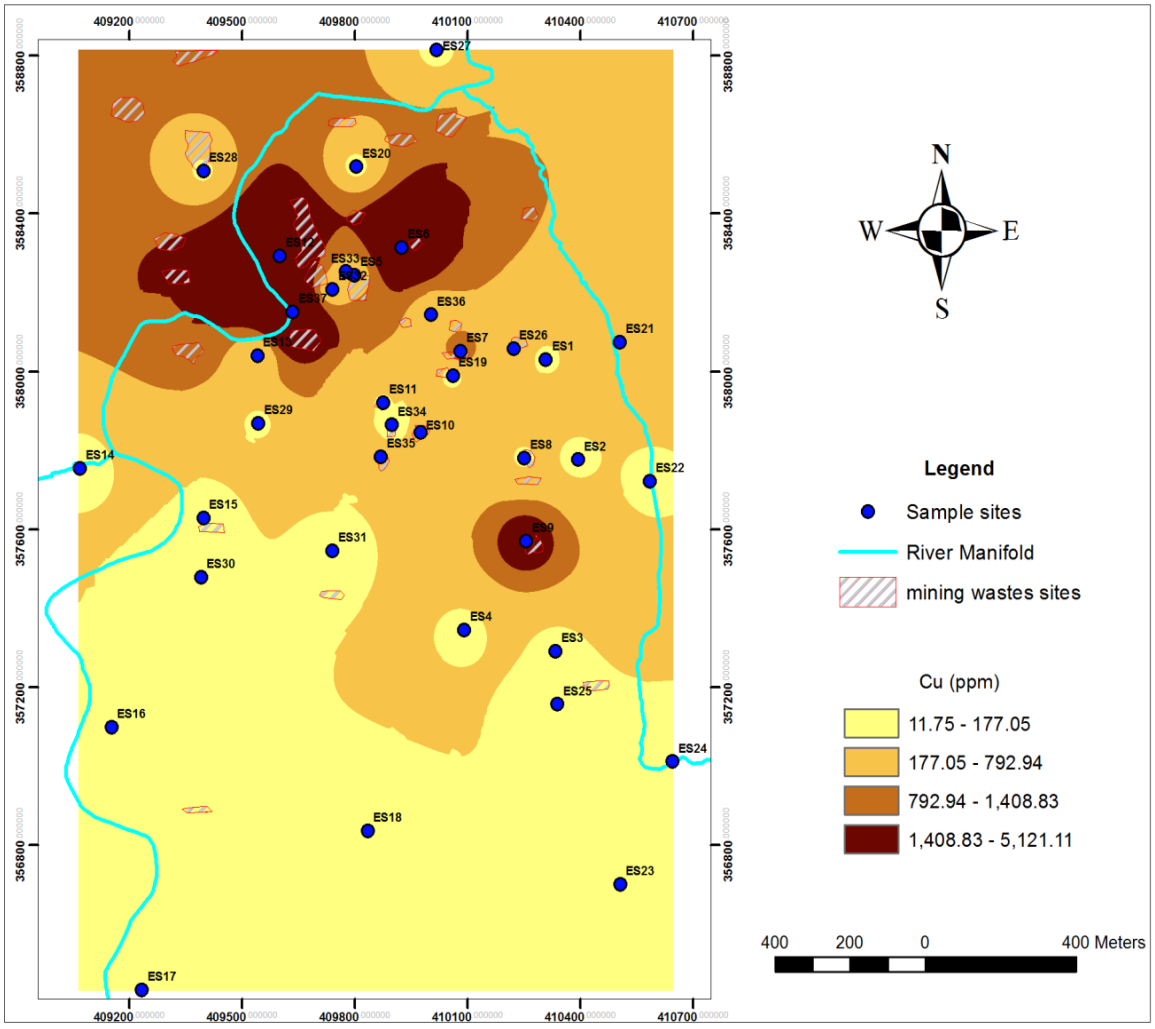
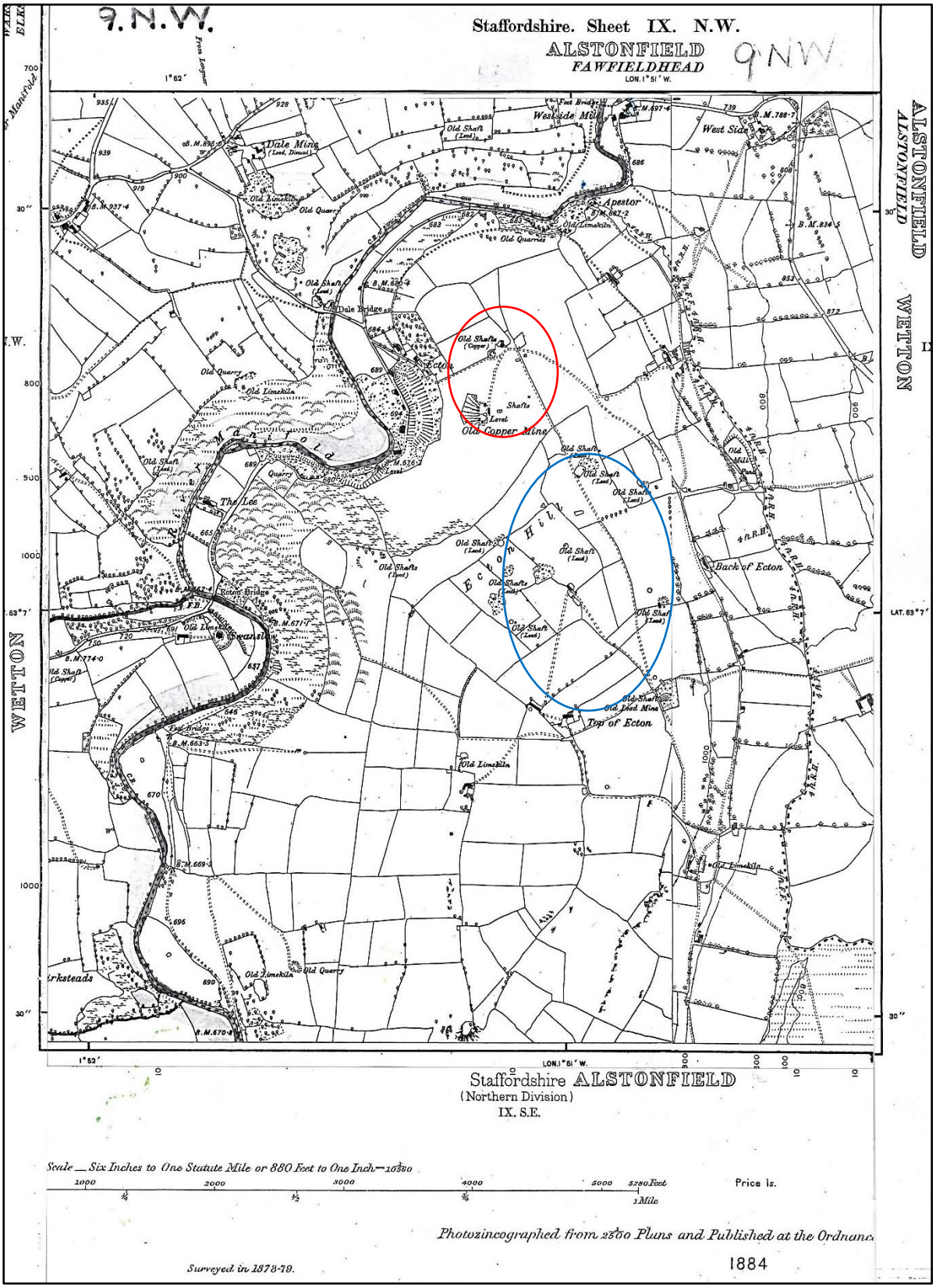


Figure 4.1: Spatial distribution of Cu in the collected soil samples over the study area


9.N.W.
Staffordshire. Sheet IX. N.W.
ALSTONFIELD
FAWFIELDHEAD
LON. 1° 51′ W.
9 NW
Dale Mine
Old Quarry
Old Limekiln
Dale Bridge
Old Shaft (Lead)
Old Shafts (Copper)
Shafts
Level
Old Copper Mine
Ecton
Manifold
The Lee
Quarry
Old Shafts (Lead)
Ecton Hill
Back of Ecton
Top of Ecton
Old Lead Mine
Old Shaft (Copper)
Rotary Bridge
Old Limekiln
Old Quarry
Old Limekiln
Old Shaft (Lead)
Old Shafts (Lead)
Old Shaft (Lead)
Old Shaft (Lead)
Old Shaft

4.2.2. Lead

The lead concentrations for the analysed soil samples ranged from 28.8 mg/kg to 36644.3 mg/kg (Table 4.1). The concentration levels of Pb for all of the collected samples were above the value of the background for limestone (i.e. 8 mg/kg) (Table 4.2). The spatial distribution of Pb across the study area is shown in figure 4.3.

It can be observed from Figure 4.3 that the highest levels of Pb (dark brown colour) were recorded approximately on the eastern side of the study area. The majority of these samples, which have elevated levels, for instance samples ES7, ES9, ES19, ES35) are located next to old Pb mines (Fig. 4.2, blue circle) where Pb was extracted during mining time. The best interpretation of these results is that anthropogenic activities (past mining operations) are responsible for these high levels. However, the distribution pattern of Pb is quite different to that of Cu with both shows high concentrations (dark brown colour) in different locations (see red and blue circles in Fig. 4.2). Suggesting that Pb has been extracted from another source different to that of Cu, and this might be mineral veins different to the ones Cu has been extracted from.

Furthermore, many researchers have demonstrated that high concentrations of lead can be found in soils around industrial sites due to the atmospheric emissions from exhaust gases and fossil fuel burning; as a result of this, the heavy metal content is deposited in the surrounding soil causing elevated concentrations of Pb and other related contaminants (Jackson, 1997; Hu *et al.,* 2013). This probably an additional input of Pb at the study area due to burning coal, as this was used to supply the required energy for the mining operations during the mining period (Barnatt, 2013).

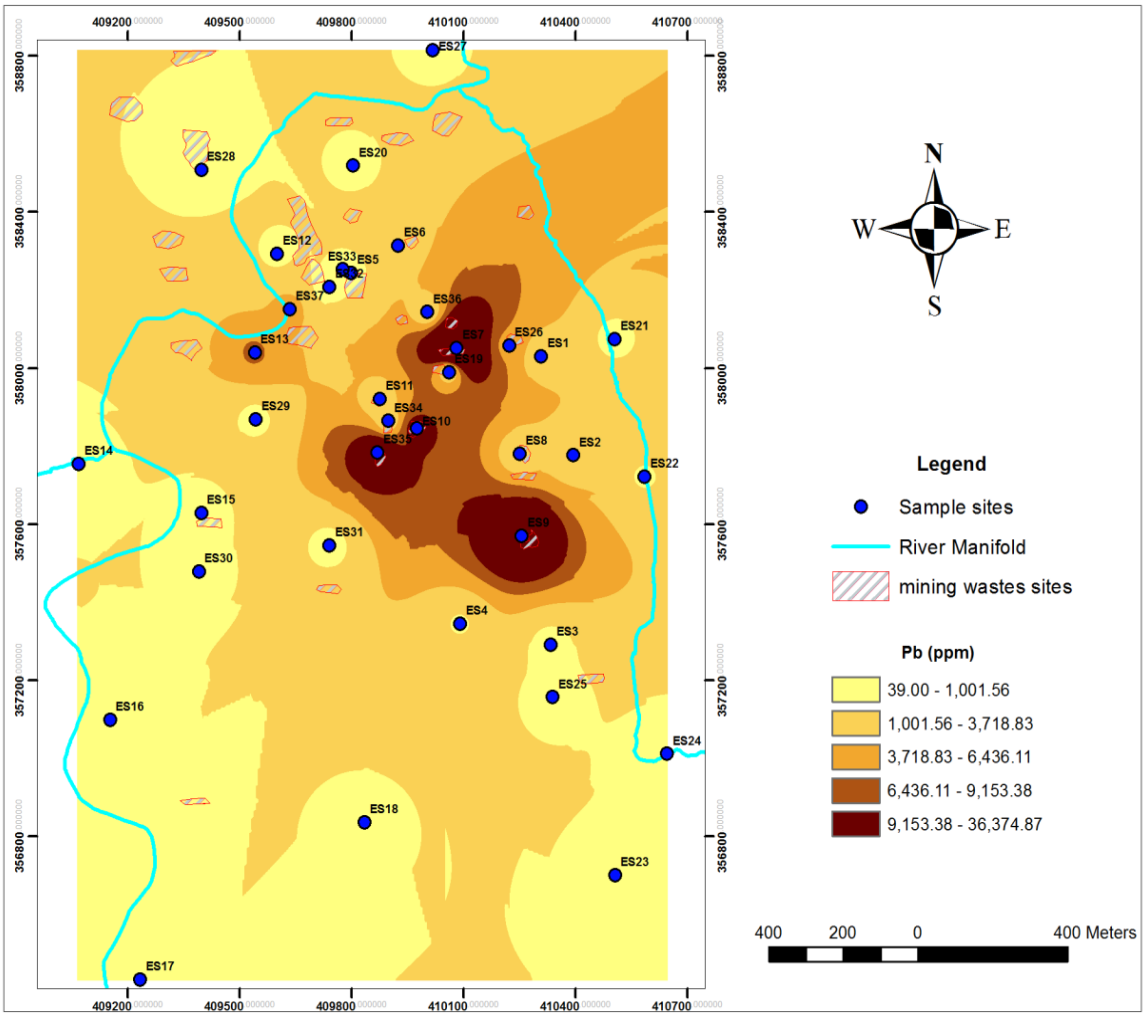


Figure 4.3: Spatial distribution map of Pb in soil samples over the study area

4.2.3. Zinc

The concentrations of zinc in the studied soil samples ranged from 68mg/kg to 14378.3 mg/kg (Table 4.1). All of the soil samples have amounts of Zn that above the background limits (i.e. 25 mg/kg) (Table 4.2). The spatial distribution map of zinc over the study area is given in figure 4.4. It can be seen that elevated amounts of Zn (dark brown colour in Fig. 4.4) have been indicated around mining wastes in two locations. In the northern part of the study area, where old Cu mines are located, by samples such as ES6, ES7, ES19 and ES39 and in the east side of the study area,

where old Pb mines are situated, by samples such as ES8 and ES 9. When superimpose the spatial distribution maps of Zn on both Cu and Pb distribution maps, it can be clearly seen that Zn is related to both Cu and Pb sources, with predominant Cu source for the majority of Zn. Therefore, Zn is most likely to have been introduced into the soil due to the former mining activities in the area when Zn was extracted from sphalerite (ZnS) as has been mentioned earlier in mining history section.

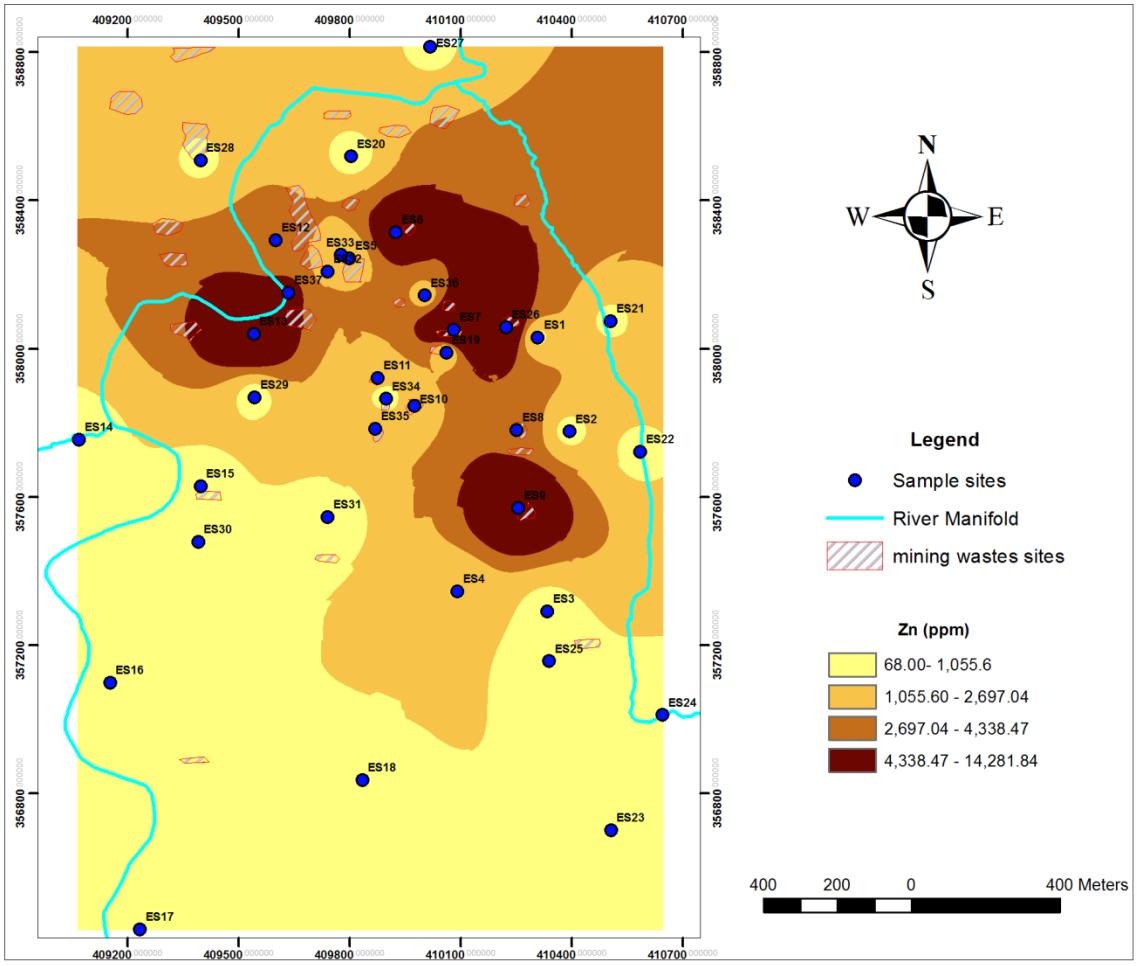


Figure 4.4: Spatial distribution map of Zn in soil samples over the study area

In addition, Alloway (1995) highlights that a possible key factor that played a significant role in the dispersal of contaminant heavy metals into soils during the mining period in the UK was the poor separation process during mining workings. Furthermore, According to (Aitkenhead, 1985), Widmerpool shale formation seen on the eastern side of Ecton Hill (refer to Fig. 2.5 and appendix N), might be an additional source of Zn as in the case of sample ES21 (Fig. 4.4) which has 660 mg/kg Zn, which is 4 times higher than the background level (4.2). It has been documented by Levinson (1979) that shale beds contain up to 100 mg/kg Zn (Table 6.2). As a result, it can be concluded that both anthropogenic activities and weathering shale beds are possible sources for Zn.

4.2.4. Manganese

In the current study, the maximum and minimum concentrations of Mn were 3478.8 mg/kg and 127.5 mg/kg, respectively (Table 4.1). A spatial distribution map of Mn is shown in Fig. 4.5. It can be seen that the spatial distribution map of Mn is similar to that of Zn to some extent with high levels recorded around mining waste sites.

Collected soil samples showed different Mn concentrations over the study area, with higher than the background level of 1100 mg/kg in limestone (Table 4.2) being recorded for samples such as ES4, ES5, ES20, ES25, ES27, ES33, ES35 and ES36. The locations of these samples are close to the old Cu and Pb mines. This may suggest that Mn is produced into the surrounding soils as by-product from Cu and Pb mining. According to Davies (1980), sulphide minerals have some amounts of heavy metals associated with as impurities such as Mn, Ni, Cr (Table 6.1). This can be confirmed by samples have levels close to those of the background value, and located away from mining waste locations such as ES14, ES17 and ES23 for which 853.25 mg/kg, 930.25 mg/kg and 520.75 mg/kg, respectively, were recorded.

Like the case of Cu, Pb, and Zn, past mining operations in the area are most likely to be the source of elevated Mn concentrations.

Also, the burning of fossil fuels, as mentioned by many researchers, such as Lu et al. (2009), is a significant anthropogenic source of heavy metals including Mn. Therefore, in the present study, coal burning is likely to be another source of Zn as coal was burned to supply the required energy for the mining operations during the mining time (Barnatt, 2013).

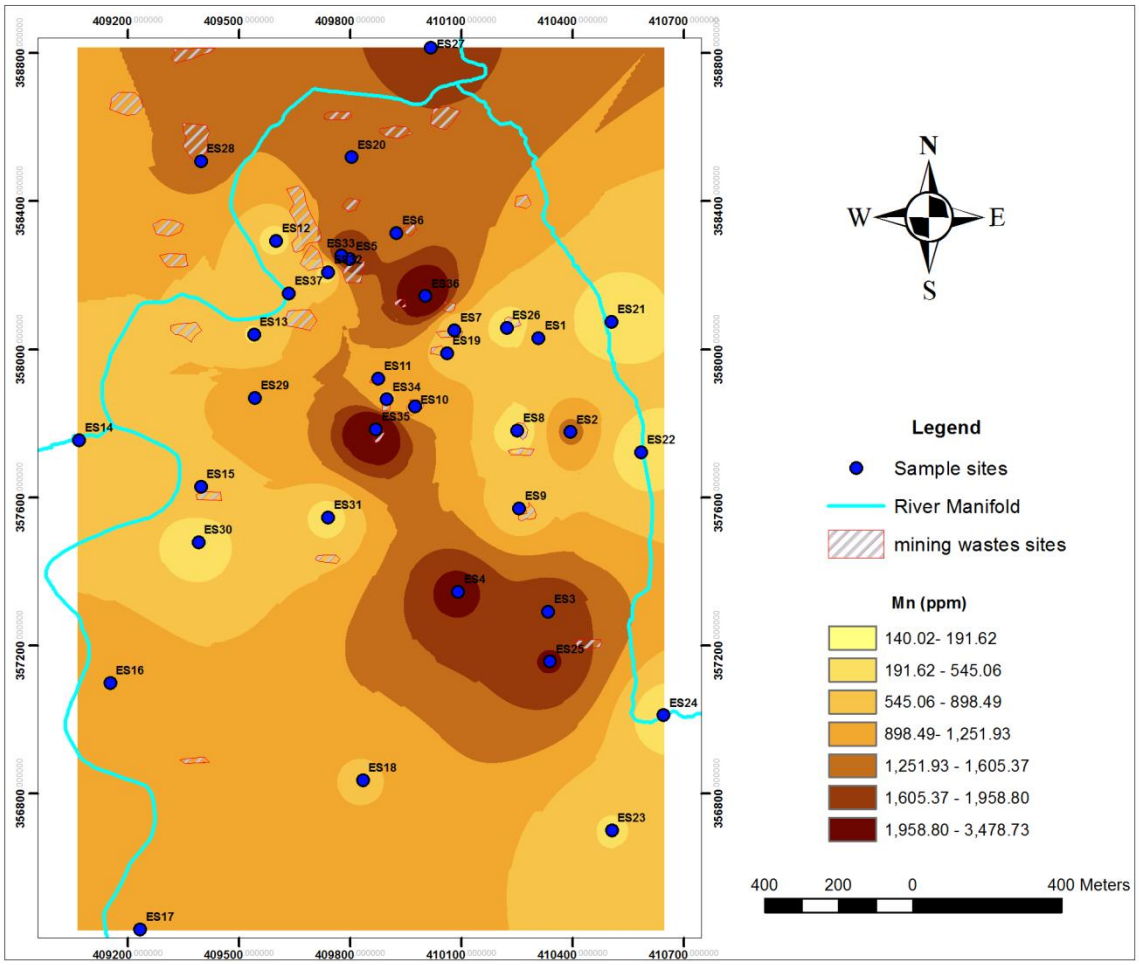


Figure 4.5: Spatial distribution map for Mn in soil samples over the study area

4.2.5. Chromium

The concentrations of Cr in the collected soil samples ranged from 1mg/kg to 99mg/kg (Table 4.1). The majority of the analysed samples were found to have levels above the limestone value (background) of 10 mg/kg.

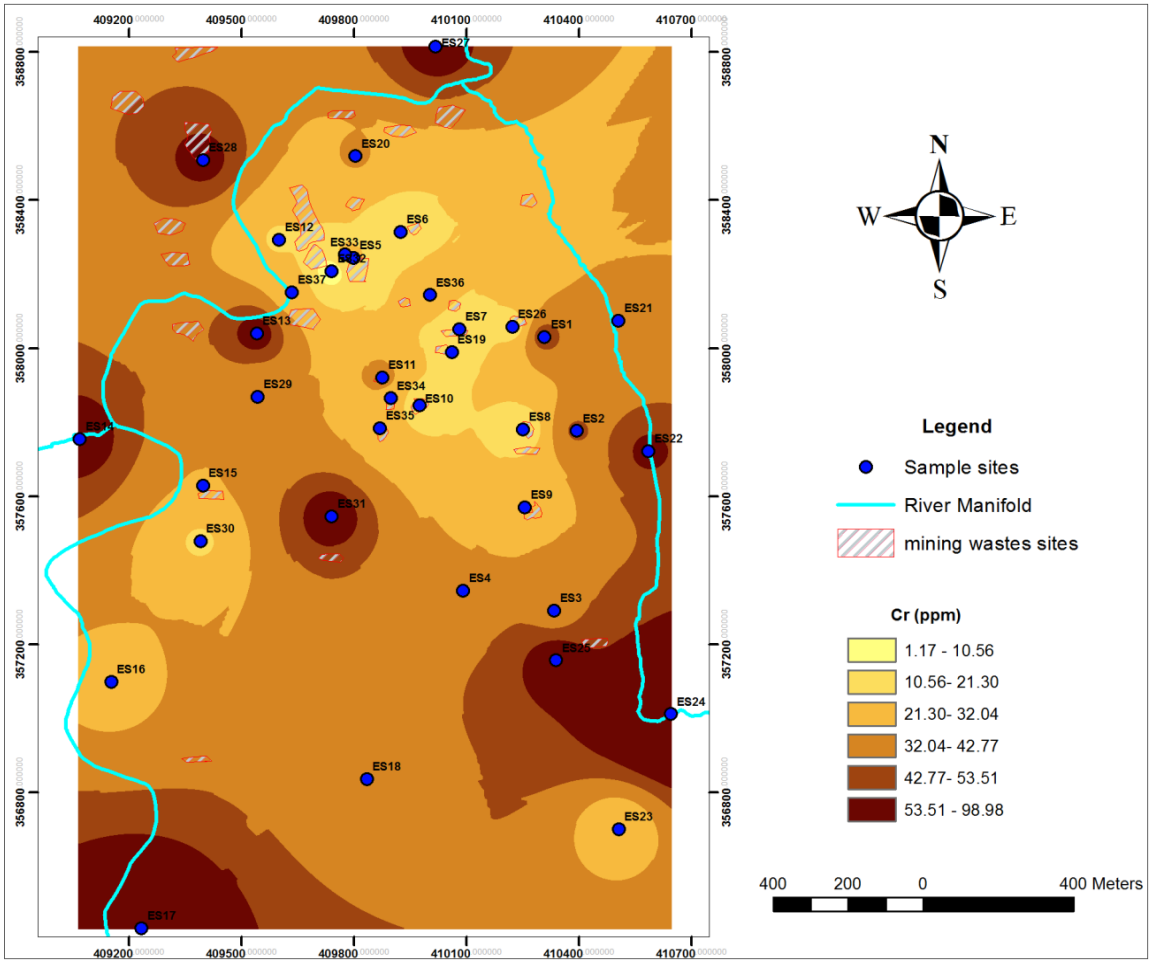


Figure 4.6: Spatial distribution map for Cr in soil samples over the study area

The spatial distribution map for Cr over the study area is shown in Fig. 4.6. From Fig. 4.6, it can be observed that there are some spots with a dark brown colour (Fig. 4.6) being distributed at different locations, at which high levels of Cr were recorded. The distribution mode of such elevated areas is different to that of Cu, Pb and Zn. This may indicate that Cr has attributed from various sources. With regard to the high

levels being recorded at the eastern part of the study area, this might suggest the natural input, which likely to be the shale outcrop seen at the east of the study area (refer to Fig. 2.1). In addition, human activities, which are former mining operations in the area, are more likely to be another source for Cr, which can be produced as by-product during mining (Davies, 1980). Moreover, as the area is being used for stock rearing, Cattle manure can contribute with a significant amount of Cr to the soil locally (Nicholson et al., 2003).

4.2.6. Nickel

The current study shows that Ni has a concentration ranging from 11.3 mg/kg to 134.8 mg/kg (Table 4.1). The concentration levels of Ni for all of the collected samples were higher than the background level of 12 mg/kg (Table 4.2), except for sample ES13, in which the concentration of Ni was 10 mg/kg. The spatial distribution map of Ni for the collected soil samples over the study area is shown in Fig. 4.7.

Frome Fig. 4.7, three spots with a dark brown colour can be recognised where high concentrations of Ni were found. The possible source of such elevated levels does not seem to be ore mining operations because the other samples from the same area did not show high concentrations, although their locations were close to the mining waste sites such as ES 5, ES25 and ES33. In addition, the area located to the east of the study area (around the sample ES 24) shows high levels with distribution pattern similar to that of Cr. This might indicate that such high levels come from a source located to the east of the area and most likely to be the shale outcrops (see Fig. 2.4)

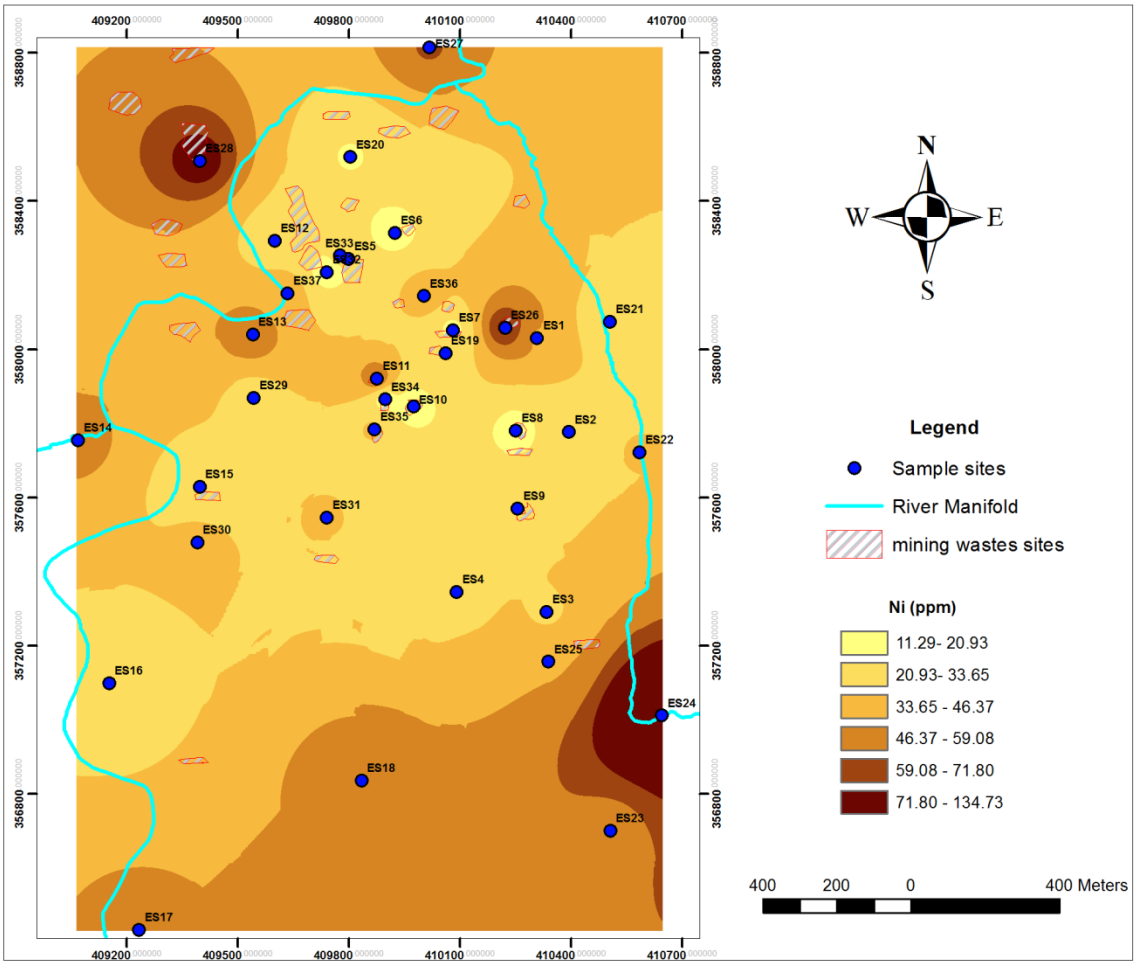


Figure 4.7: Spatial distribution of Ni in soil samples over study area

Therefore, a natural source is the best interpretation for such levels, although an anthropogenic source (e.g. combustion of fuel and coal) could be an additional input, as mentioned by Reimann and De Caritat (1998). One of the most significant sources of Ni is the burning of fossil fuels. Therefore, burning of coal might be an anthropogenic source for Ni to the soil of the area as coal, as has been previously noted, was used to supply the required energy during the mining period and for a long time (Barnatt, 2013).

4.2.7. Vanadium

In the current study, the concentrations of V were found to be in the range of 0.5 mg/kg to 114 mg/kg (Table 4.1). All of the collected soil samples were found to have concentration levels of V more than the amount of the background (limestone) of (20mg/kg), except for samples ES6, ES7, ES8, ES10, ES18, ES28, ES32, and ES34 for which 16.75 mg/kg, 13.25 mg/kg, 15.5mg/kg, 13.25, 16.5mg/kg, 16 mg/kg, 0.5 mg/kg and 14 mg/kg were recorded, respectively. The spatial distribution map of V over the study area is shown in Fig. 4.8.

From Fig. 4.8, it can be seen that the highest concentrations of V were located on the eastern side of the study area (dark brown colour). However, lower concentrations were found around mining wastes. Therefore, as in the case of Ni, it can be concluded that the possible source of such levels is most likely to be natural weathering of surrounding rocks, which are most likely to be the weathering of shale beds that located at the east of the study area (refer to Fig. 2.4). According to Davies (1983), shale, which is recognised by its black and dark colour due to the large amount of sulphide minerals and organic matter it contains, has high levels of U, Cu, Pb, Zn, Cd, Au, V, Mo and just a small outcrop of it in the area can make unusual metal levels. Similar results for V concentrations have been recorded elsewhere by other researchers, for example Sourosh *et al*. (2015).

Overall, from the spatial distribution maps for all of the studied heavy metals (i.e. Cu, Pb, Zn, Mn, Cr, Ni, and V), it can be observed that Cu, Pb, Zn and Mn have to some extent a similar pattern of spatial distribution over the study area with elevated concentrations have been recorded close to mining wastes sites, suggesting an anthropogenic input for such levels

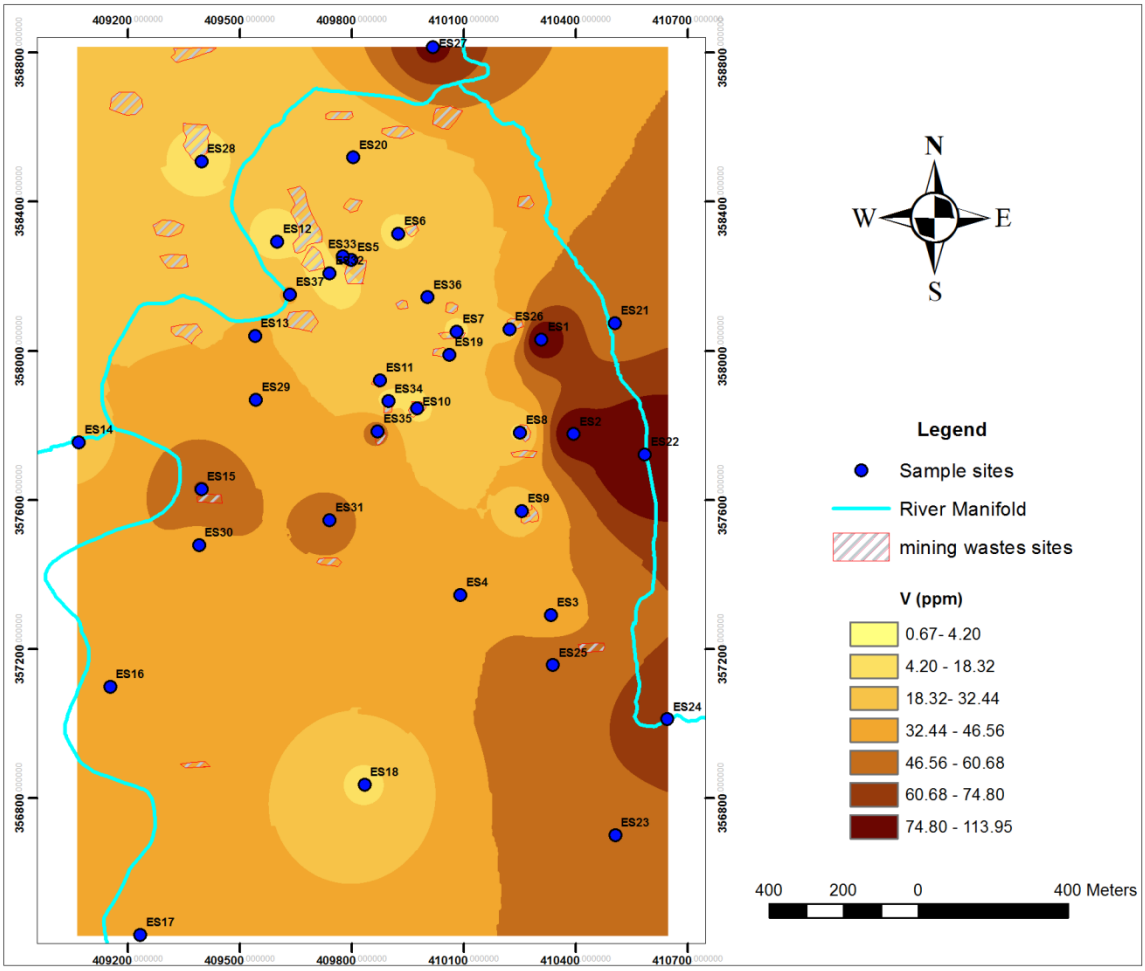


Figure 4.8: Spatial distribution of V in collected soil samples across study area

Hoverer, in the case of Ni and V, these metals have recorded high concentrations located at the eastern boundary of the study area and such high levels are likely attributed to the shale outcrops located at the eastern edge of the area. Spatial distribution map of Cr reveals that this element has a different distribution pattern with possible source being mixed.

4.3. Heavy metal contamination assessment at Ecton mining area

Soil heavy metal pollution has become a problem of great concern worldwide. These chemical elements have been introduced into environment from different sources and their emission levels depend on the physico- chemical properties (Harrison, 2001). As a result the evaluation of such pollution is very important in order to identify the extent to which a particular area has been polluted, as this will help to put

a suitable plan for remediation into action. To achieve this task, many methods have been used by different researchers, and in the current study the following approaches have been applied to assess the contamination of soil in the study area.

4.3.1. Evaluation of heavy metal contamination using the geoaccumulation index (I_{geo}) of Muller

This approach is a well-known method in the field of contamination assessment and has been used by many researchers (e.g. Saleem *et al*., 2015; Bai *et al*., 2012; Lu *et al.*, 2009). In this study this method has been utilised. It shows the degree of metal contamination by dividing the current concentration of the metal of interest by its background using the following equation (1) (Forstner and Muller, 1981):

$$\mathbf{I_{geo}} = \log_2 (P_i/1.5*P_{iback}) \quad (1)$$

Where p_i is the measured concentration of the studied heavy metal, and p_{iabck} is the background amount of the heavy metal. The constant number (i.e. 1.5) is a factor of background correction because of lithology effect. According to the authors mentioned above, the geoaccumulation index (I_{geo}) has been classified into seven classes (Table 4.3), starting from class 0 (uncontaminated), and ending with class 6 (extremely contaminated).

Table 4.3: Showing Muller's geoaccumulation index and different contamination classes (adapted from Forstner and Muller, 1981).

I_{geo} classes	I_{geo} index	Contamination degree
0	**<**0	Uncontaminated
1	0-1	Uncontaminated/moderately contaminated
2	1-2	Moderately contaminated
3	2-3	Moderately contaminated/ strongly contaminated
4	3-4	Strongly contaminated
5	4-5	Strongly contaminated/extremely contaminated
6	**>**5	Extremely contaminated

The geoaccumulation indexes (I_{geo}) for all of the samples were first calculated using the Muller equation, and then presented separately for the soil samples and the floodplain samples, as shown in Fig. 4.8, and Fig. 4.9, respectively. Then, the total evaluation of heavy metal contamination was carried out for all the collected samples using the average amount of (I_{geo}) for all of the metals so that the different (I_{geo}) classes of pollution (Table 4.4) can be indicated.

It can be seen that among all of the studied metals, lead had the highest amount of contamination, which was classified as extremely contaminated (i.e. class 6) in both soil samples and floodplain samples (Table 4.4). Therefore, depending on the amount of the geoaccumulation index (I_{geo}), lead is seem to be the most harmful element as it has a peak I_{geo} value of about 13 in samples ES7 and ES10 (Fig. 4.8).

Regarding the level of contamination with Cu, the degree of contamination ranged from class 4 (i.e. strongly contaminated) in the floodplain samples to class 5 (i.e. strongly contaminated / extremely contaminated) in the soil sample (Table 4.4), and reached its highest value, of approximately 8.5 in samples ES6, ES32 and ES33 (Fig. 4.8). However, the geoaccumulation index values (I_{geo}) for Zn extended from class 5 (i.e. strongly contaminated/ extremely contaminated) in the floodplain samples to class 6 (extremely contaminated) in the soil samples and reached their peak value of almost 9.5 in sample ES7 (Fig. 4.8).

All of the other investigated elements (i.e. Ni, Mn, Cr, and V), based on the calculated geoaccumulation index (I_{geo}), show the same contamination levels in both soil samples and floodplain samples. With regards to Ni and V contamination levels, both elements demonstrate a contamination level of class 2 (i.e. moderately contaminated) in both the floodplain and soil samples. However, Mn and Cr show

contamination levels of uncontaminated/moderately contaminated (i.e. class 1) and moderately contaminated (i.e. class 2), respectively, in both the soil and floodplain samples (Figures 4.9 and 4.10) (Table 4.4).

Table 4.4: Geoaccumulation index classes for studied metals at the study area

Samples types	**V**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Pb**
Soil samples (n=37)	Class 2	Class 3	Class 1	Class 2	Class 5	Class 6	Class 6
Flood plain samples (n=11)	Class 2	Class 3	Class 1	Class 2	Class 4	Class 5	Class 6

Overall, depending on the calculated average geoaccumulation index classes, the degree of contamination of the collected samples was found to be in the following order:

Pb=Zn>Cu>Cr>Ni=V>Mn and Pb>Zn>Cu>Cr>Ni=V>Mn, for the soil samples and floodplain samples, respectively. It can be concluded that the elevated concentrations of Cu, Pb, and Zn in the studied samples are more likely attributed to the former mining activities, as this area (Ecton area) was mined for a long time for the production of copper, lead, and zinc. As a result the concentrations of these metals have become elevated due to the disposal of mining waste into the surrounding environment (Bradley and Cox, 1986; Robey & Porter, 1972; Harris, 1971; Geeson *et al*., 1998).

Finally, It is worth noting that is some soil samples such as (ES2, ES7, ES12, ES21, ES22, ES22, ES23, ES24, ES26, ES30 and ES31 (Fig. 4.9) a negative geoaccumulation index values were recorded, such values indicate that soils at these sites are uncontaminated with Mn (class 0) (refer to Table 4.3).

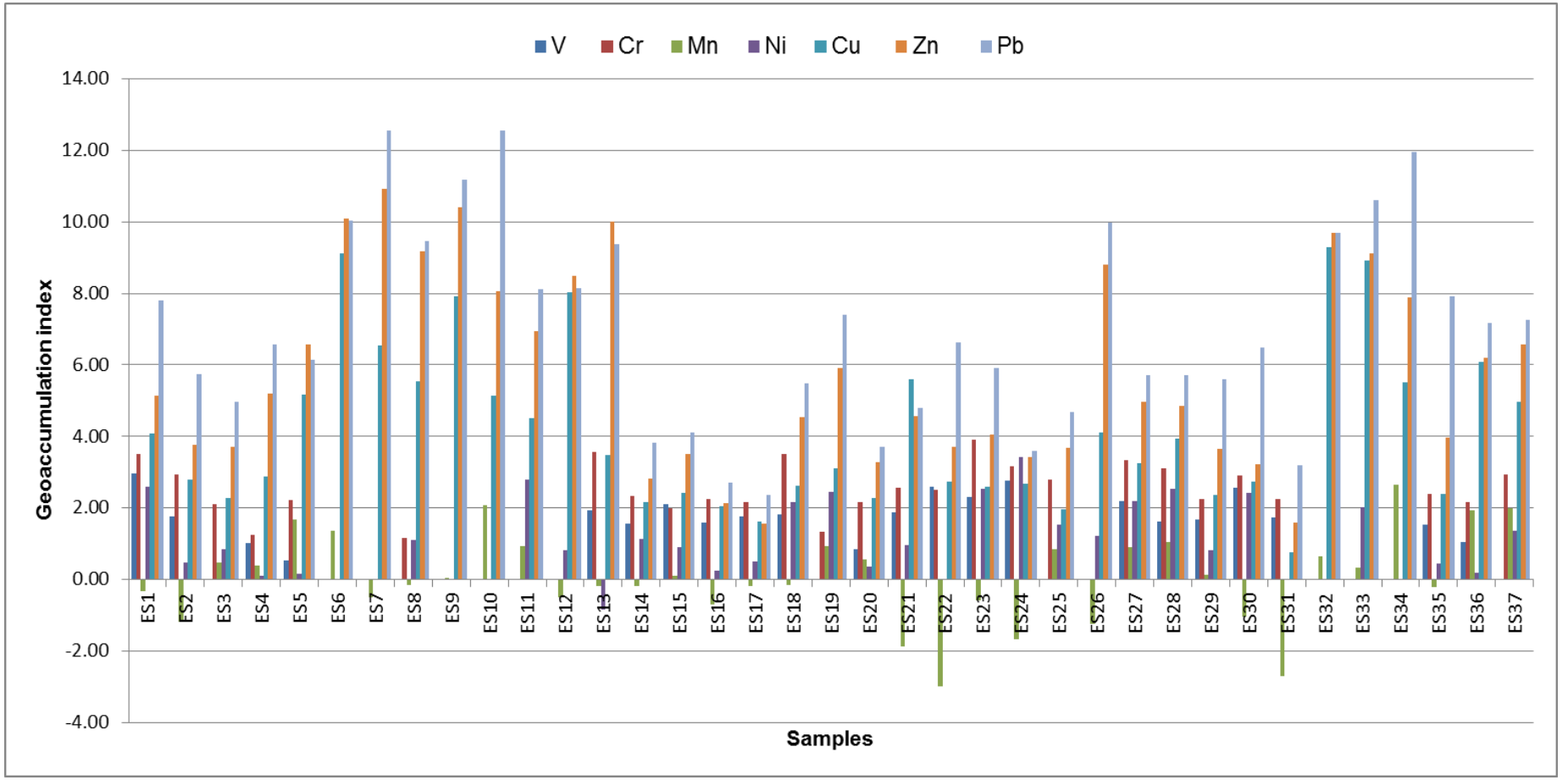


Figure 4.9: Muller geoaccumulation indexes of heavy metal contamination in soil samples at the study area

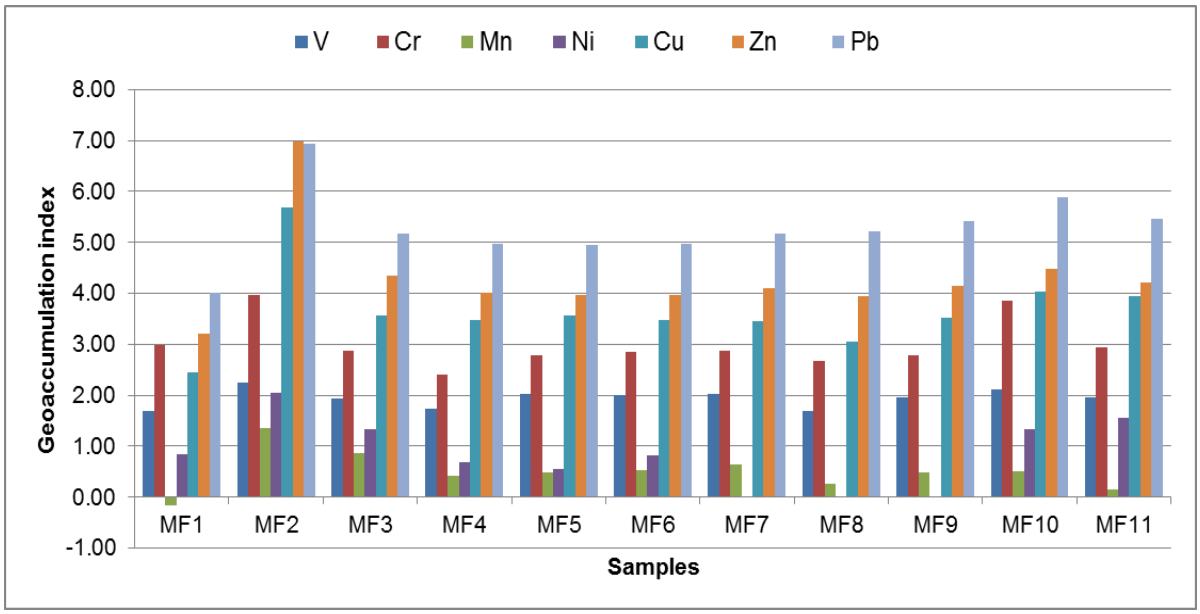


Figure 4.10: Muller geoaccumulation indexes of heavy metal contamination in the River Manifold flood plain samples at the study area

4.3.2. Potential ecological risk assessment

Evaluation of the potential ecological risk for the area of interest is very important as it gives valuable data to investigate and predict the risk that soil contaminants can pose to human health and the surrounding environment (Wei and Yang, 2010). Regarding the potential ecological risk assessment, various approaches have been used by different researchers to perform this task, for example the enrichment factor (EF) by Salmanighhabeshi et al. (2015), the contamination factor (Cf) by Hakanson (1980), and the integrated pollution index (IPI) by Yahlah- Abanuz, (2011). In this study the enrichment factor (EF) method was used to estimate the potential ecological risk of the investigated soil pollutants in the study area. The reason of choosing this approach is that, since the background value is a significant factor for estimating the potential ecological risk. Therefore the results of applying this

approach are expected to be accurate as the background of the current study is quite clear (i.e. limestone).

To apply this method, first of all the concentrations of the metals of interest have to be normalised using reference elements (i.e. Fe, Sc, Ti, Al, Ca, and Mn) (Yaylah-Abanuz, 2011). In the current study, Mn was used as a reference element for standardisation, as this element has been commonly used for the estimation of the enrichment factor (Quevauviller, 1989). The amount of the enrichment factor (EF) for the studied metals was found using the following equation (2):

$$EF = [C_n \text{ (sample)} / (C_{ref} \text{ (sample)}] / [B_n \text{ (background)} / (B_{ref} \text{ (background)}] \quad (2)$$

Where: C_n is the measured concentration of the element in the sample, C_{ref} is the concentration of the reference element (i.e. Mn) in the sample, and B_n and B_{ref} are the background concentrations of the element and the reference metal, respectively (Wedepohl, 1995).

According to Sutherland (2000), based on this method the calculated enrichment factor amounts are categorised into five groups of enrichment (Table 4.5).

To find out the potential environmental risk for the studied metals, the enrichment factor (EF) method was used and the average amounts in the soil and floodplain samples of the study area are shown in Table 4.6 and illustrated in Figure 4.11.

Table 4.5: Ecological risk assessment groups using enrichment factor (EF)

Enrichment groups	Enrichment factor (EF)	Enrichment degree
1	EF < 2	Deficiency to minimal enrichment
2	2 ≤ EF < 5	Moderate of enrichment
3	5 ≤ EF < 20	Significant enrichment
4	20≤EF< 40	Very high enrichment
5	EF≥40	Extremely high enrichment

Table 4.6: Average amount of enrichment factor (EF) for studied heavy metals

Sample types	V	Cr	Mn	Ni	Cu	Zn	Pb
Soil samples (n=37)	7.84	10.52	1.00	4.01	62.25	261.62	593.43
Flood plain samples (n=11)	2.76	5.90	1.00	1.25	9.53	15.84	29.03

Based on the calculated enrichment factor, it can be seen that among the metals studied the average amount of the enrichment factor (EF) for Pb was the highest followed by zinc and copper (Fig. 4.10). However, the potential environmental risk of Pb, Cu, and Zn was found to be nearly the same and ranged from significant enrichment (group3) in the floodplain samples to extremely high enrichment (group 5) in the soil samples, except for Pb, which reveals a pollution level of very high enrichment (group 4) in the soil samples (Table 4.7).

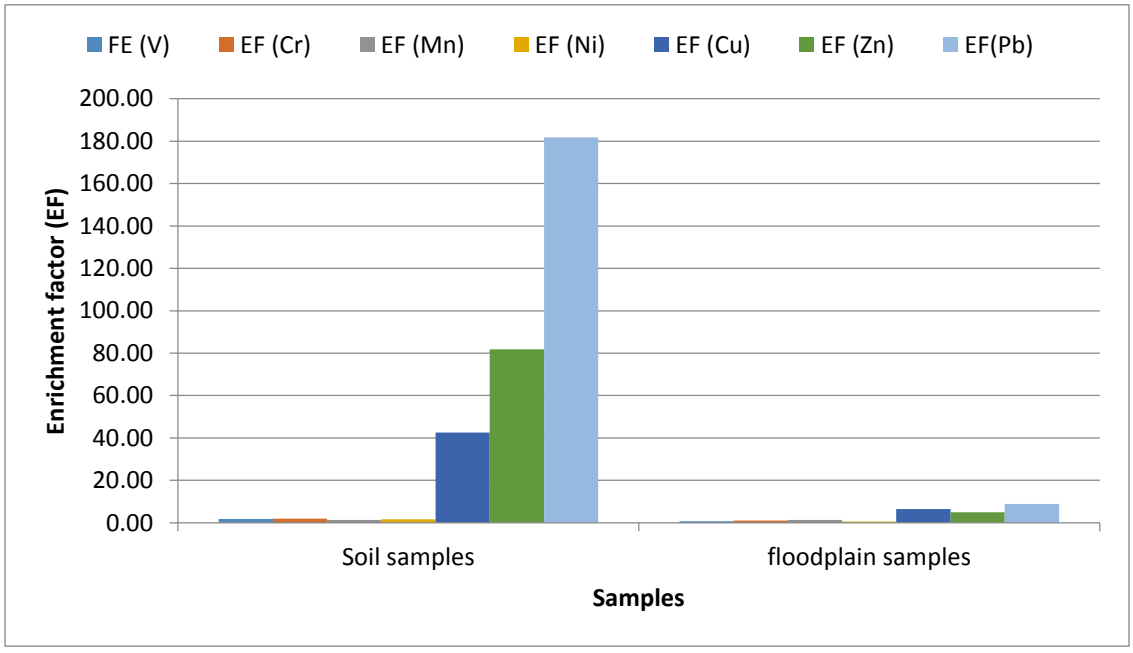


Figure 4.11: Calculated average enrichment factor (EF) for both soil and floodplain samples collected from the study area

Regarding the enrichment degree of Cr and V, both elements show a significant enrichment degree (group 3) in both the soil and floodplain sample, except the floodplain samples for which V demonstrates a moderate enrichment level (class 2). However, the lowest enrichment degree was revealed by Ni and Mn in both the soil and floodplain samples with an enrichment level of Deficiency to minimal (class 1), except Ni which shows a moderate enrichment degree (class 2) in soil samples studied (Table 4.7).

On the basis of the calculated levels of the enrichment factor (EF), the levels of the potential ecological risk that metals studied can pose to the environment are in the following order: Pb=Zn=Cu>Cr=V>Ni>Mn for the soil samples and Pb>Cu=Zn=Cr>V>Mn=Ni for the floodplain samples.

Overall, the highest levels of the enrichment factor (contamination) in the studied samples were found mainly in the case of Pb, Cu, and Zn (Table 4.7). The possible source of such levels is likely to be anthropogenic as this area was used for mining to extract the aforementioned metals and for a long periods (refer to mining history section in chap. 2), as has been pointed out by many researchers, such as Ixer and Vaughan (1993), Ineson and Ford (1982), Bradley and Cox (1986) and Robey & Porter (1972). As a consequence, high amounts of these metals had disposed of into the area resulting in high enrichment degree to be recorded.

Table 4.7: Potential ecological risk assessment using the enrichment factor (EF) approach for studied heavy metals in the study area.

Samples types	V	Cr	Mn	Ni	Cu	Zn	Pb
Soil samples (n=37)	3	3	1	2	5	5	5
Flood plain samples (n=11)	2	3	1	1	3	3	4

Finally, as in the current study two methods (i.e. geoaccumulation index (I_{geo}) and enrichment factors (EF) were utilised to assess the level of contamination in the study area, it would be worth finding out how the results of these two methods are correlated. The average values for I_{geo} and the EF indexes are shown in Table (4.8).

Table 4.8: Mean values for calculated geoaccumulation index and enrichment factor for the study area

Studied elements	**V**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Pb**
Geoaccumulation Index($I_{geo)}$	7.84	10.52	1.00	4.01	62.25	261.62	593.43
Enrichment factor (EF)	2.76	5.90	1.00	1.25	9.53	15.84	29.03

It can be seen that there is a fairly strong correlation between the values of the I_{geo} index and EF (Fig. 4.12) with a correlation coefficient of R^2= 0.7617, suggesting that the results of both methods are linked with an acceptable result. Therefore, both methods present a similar environmental data in terms of ecological assessment. As a result, both are reliable for such an assessment. Similar findings were found by other researchers elsewhere, such as Salamanighbashi *et al*. (2015), who investigated the pollution coming from some selected heavy metals, similar to those of our study, in an area affected by mining activities in Chile.

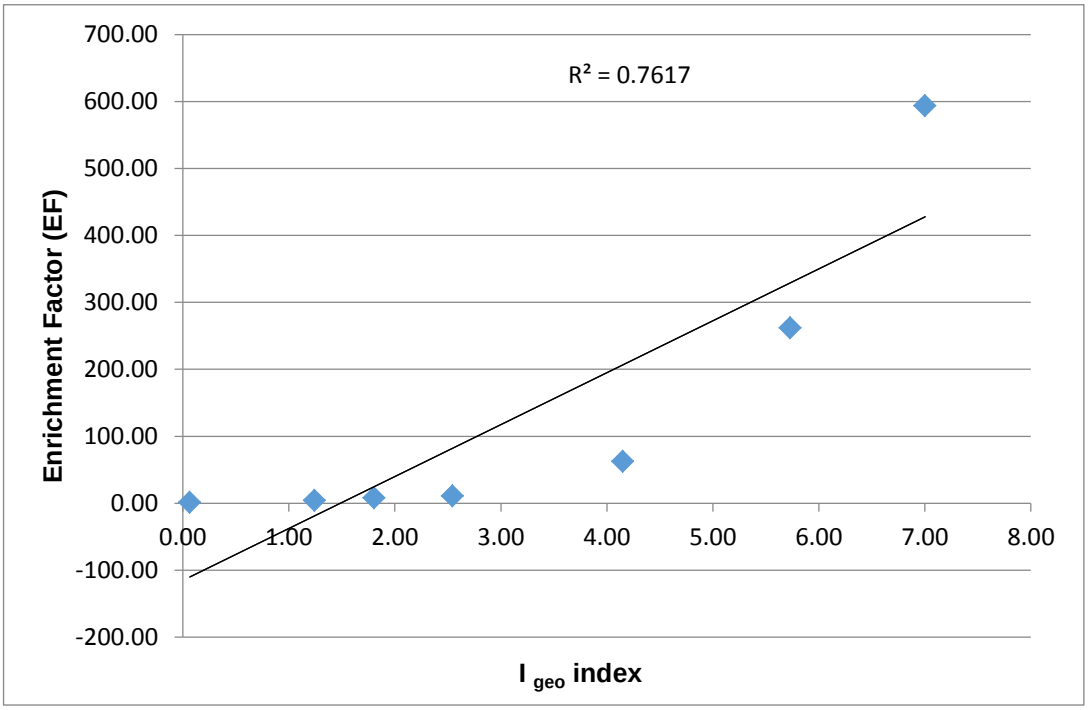


Figure 4.12: Correlation between geoaccumulation index and enrichment factor (the two methods have been used for contamination assessment).

4.3.3. Heavy metal concentrations assessment for different land uses

As has been previously mentioned, the study area was mined for extraction Cu, Pb and Zn (refer to mining history section in chap. 2), therefore it will be useful to assess the levels of these metals for various land usages. In section (1.6) the UK regulations regarding heavy metal concentrations in soils have been discussed and the interdepartmental committee on the development of contaminated land (ICRCL) has published the first guidance to monitor the levels of some contaminants in contaminated soils. These levels are called threshold trigger values, which can be defined as levels above which the soils are considered to be contaminated to the point that they could harm living organisms, and action must be taken. However, soils with amounts of heavy metals below the threshold trigger values are considered to be uncontaminated and no action is required to be taken (ICRCL, 1990).

After that, new levels have been introduced by the Environment Agency and DEFRA as an attempt to give a scientific framework for assessment the level of land contamination. These values are called Soil Guideline Values (SGVs) for Contaminated Land Exposure Assessment (CLEA). According to Department of Environment (2002b), SGV can be defined as values at which particular contaminants can pose a threat to human health for a specific land use.

In this section the results of heavy metal concentration will be assessed for different land uses by comparing the results of the current study with the UK government guidelines. Since the study area is currently used for stock rearing and agricultural purposes, therefore ICRCL guideline (Table 1.4) values will be used for such assessing along with the CLEA soil guideline levels (SGV) (Table 1.5) supposing that the area will be used in future for purposes such as residential, allotments and commercial.

To this end, the concentrations of metals being studied for both soil and floodplain samples along with the ICRCL and CLEA soil guideline levels have been gathered together (Table 4.9) as this will make the comparison easier.

With regards to soil samples, compared with ICRCL guideline values, it can be seen that the average amounts of Cu, Pb and Zn are higher that the ICRCL values for both grazing livestock and crop growing (Table 4.9). As a result, there could be a significant risk to grazing animal and crop growing on those soils, and hence the phytotoxicity and risks to grazing livestock should be of concern due to such levels.

Table 4.9: Assessment of heavy metal concentrations for different land purposes using the UK soil guideline values (mg/kg) (gathered from tables 1.4 and 1.5)

Soil types	Cu	Pb	Zn	Mn	Cr	Ni	V
Soil samples (n=37)	1679.6	8578.1	9611.2	2430.6	97.8	55.0	114.1
Floodplain samples (n=11)	337.1	530.5	1003.5	2416.3	126.5	39.3	115.8
ICRCL trigger values for grazing livestock	500	1000	3000				
ICRCL trigger values for crop growing	250	-	1000				
ICRCL trigger values for domestic gardens and allotment	130	500	300				
ICRCL trigger values for parks and recreational areas	130	2000	300				
CLEA's SGV for residential with plant uptake		450			130	50	
CLEA's SGV for allotments		450			200	50	
CLEA's SGV for residential without plant uptake		450				75	
Commercial /industrial		750				5000	

Likewise, the average concentrations of Cu, Pb, Zn exceed the ICRCL values suggested for domestic gardens and allotments (130 mg/kg for Cu, 500 mg/kg for Pb and 300 mg/kg for Zn), and values for parks and recreational areas (130 mg/kg for Cu, 2000 mg/kg for Pb and 300 kg/kg for Zn). As a consequence, on the basis of the current values of Cu, Pb and Zn, the land of the study area is not suitable for the purpose of domestic gardens, allotments, parks, and as recreational areas.

Compared with CLEA soil guideline values, Pb average amount (8578.1) is much higher than the CLEA values for residential with plant uptake, allotments, residential without plant uptake, and commercial uses. Therefore, based on the CLEA soil value for Pb, the area is not recommended for the land uses mentioned above. However, Cr and Ni concentrations should not be of concern for residential with plant uptake

and allotments as their mean concentrations are less that SGVs for these purposes. Similarly, Ni mean value is also not concern for both land usages (residential without plant uptake and commercial/industrial usages.

In terms of floodplain samples, Cu, Pb and Zn average values are lower than the ICRCL values for grazing livestock of (500 mg/kg, 1000mg/kg, and 3000 mg/kg, respectively) (Table 4.9) and hence, these metals should not be of concern for this purpose. However, these metals have average concentrations higher than the ICRCL trigger values for all other purposes (i.e. allotments, domestic gardens, parks, recreational areas, and crop growing), except for Pb which has an average level less than the ICRCL value recommended for parks and recreational area (2000 mg/kg).

On the basis of CLEA SGVs values, it can be seen that Pb average value (530.5 mg/kg) exceeds the levels recommended for all the purposes except for the commercial /industrial use (750 mg/kg). Ni average value (39.3 mg/kg) is lower than the CLEA SGVs values for all the recommended purposes, and hence, it is quite different for that of the soil samples as mentioned before. However, Cr concentration, based on the CLEA SGVs, is as in the case of the soil samples, should not be of concern for different land uses.

Generally, it can be concluded that, on the basis of the ICRCL trigger values recommended for different land uses, Cu, Pb and Zn average values exceed the levels for all the purposes for both soil and floodplain samples, except for floodplain samples for which Cu, Pb and Zn are recommended for the grazing livestock, park and recreational purposes. However, when comparing with CLEA SGVs levels, Cr and Pb have shown the same usages in both soil and floodplain samples, except Pb which shows level suitable for commercial/industrial purpose in the case of the

floodplain samples. Finally, while Ni average value is higher than the CLEA values for all the land usages for the soil samples, it was lower in the case of the floodplain samples, except in the case of the commercial/ industrial usage for which Ni was recommended in both soil and floodplain samples.

4.4. Summary

Spatial distribution maps of metals being studied (i.e. Cu, Pb, Zn, Mn, Cr, Ni and) has been created using the GIS approach. Different metals have shown different spatial distribution forms. Cu, Pb, and Zn exhibit elevated concentrations close to the mining waste sites, suggesting a possible anthropogenic source of these metals, which is most likely attributed to the former mining activities in the area. However, Cr, Ni and V reveal high concentration being recorded at the east side of the study area. Such levels have been thought to be from the weathering of shale outcrop located at the east of the Ecton Hill. Regarding Mn, This element shows a spatial distribution map similar to that of Zn, indicating that this metal seems to have been produced as by-product from previous mining workings. In addition, all the metals studied show total concentrations higher than their background level (limestone) for the majority of the soil samples collected. As a result, the former mining activities might be responsible for such elevated levels, along with natural sources (genogenic) for Ni, Cr and V.

With respect to the degree of contamination, the levels of contamination were evaluated using the geoaccumulation indexes (I_{geo}) and the enrichment factor (EF). Results indicate that, on the basis of geoaccumulation index, the degree of contamination of the collected samples was found to be in the following order:

Pb=Zn>Cu>Cr>Ni=V>Mn and Pb>Zn>Cu>Cr>Ni=V>Mn, for the soil samples and floodplain samples, respectively. However, Based on the calculated enrichment factor the levels of the potential ecological risk that metals studied can pose to the environment are in the following order: Pb=Zn=Cu>Cr=V>Ni>Mn for the soil samples and Pb>Cu=Zn=Cr>V>Mn=Ni for the floodplain samples.

Finally, validation of both methods' results (geoaccumulation index and enrichment factor) has been tested by indicating the possible relationship between them. Results reveal that there is a fairly strong association between both methods with a correlation coefficient of (R^2 = 0.7617), suggesting that the results of both methods are reliable for contamination assessment.

Heavy metals concentrations for the collected soil and floodplain samples were assessed for different land uses using both ICRCL and CLEA soil guidelines. On the basis of the ICRCL trigger values recommended for different land uses, Cu, Pb and Zn average values exceed the levels for all the purposes for both soil and floodplain samples, except for floodplain samples for which Cu, Pb and Zn are recommended for the grazing livestock, park and recreational purposes. However, when using CLEA SGVs levels, Cr and Pb have shown the same usages in both soil and floodplain samples, except Pb which shows level suitable for commercial/industrial purpose in the case of the floodplain samples. Ni average value is higher than the CLEA values for all the land usages for the soil samples, whereas, it was lower in the case of the floodplain samples, except in the case of the commercial/ industrial use.

Chapter Five: Bioavailability of selected heavy metals in the topsoil and floodplain samples from the Ecton mining area

5.1. Introduction

Generally, the bioavailability of heavy metals can be defined as the amount of metal that can be taken by organisms (humans, animals, and plants) (Adriano *et al*., 2004). In this chapter factors influencing solubility and bioavailability would be reviewed first. This will be followed by the measuring and assessing the bioavailable fraction of metals being studied.

5.2. Factors influencing the bioavailability and solubility of heavy metals in soil and sediments

Metals are found in the soil in different forms. One of the most important methods to determine these species is sequential extraction. The solubility of metals is very important in this process, and it is crucial to understand the factors that control the solubility and therefore association of metals to soils. These factors are discussed below.

5.2.1. Organic matter

In soil contaminated with heavy metals, organic matter is of great interest as it has the ability to absorb heavy metals due to its affinity to making complexes with pollutants, and high capacity for cation exchange (Alloway, 1995b). In fact, the composition of organic matter is not completely known, but it is commonly characterised by large molecular compounds (humin and humic acid), and small molecular compounds (fulvic acid) (Ross, 1996a).

In terms of solubility, humic acids tend to be soluble in water at high pH values but are precipitated at a pH value of 2. Fulvic acids are soluble in water in both acidic and basic solutions. However, humin are insoluble in water in all pH ranges (Alloway,

1995b). The different solubility of organic matter constituents in soil will show various effects on metal solubility. Organic matter content in soil is very important because it increases the surface area, and its functional groups influence the stability and fertility of soil (Shuman *et al.,* 2002). There are various sources of organic matter in soils, including the broken down products of organism remains (plant, animals), animal manure, poultry litter, and pig slurry. Long periods of application of these materials might lead to an increase in the soil abundance of heavy metals (Narwal and Singh, 1998; Weber and Karczewska, 2004). The importance of heavy metals in soil has been pointed out by many researchers. For instance, Sauve *et al.* (2000) highlight that a strong relationship between organic matter and the solubility of heavy metals is found, but that other factor such as soil pH and calcium concentration can also affect the metal solubility. When calcium is found in high concentrations, this may lead to the coagulating of dissolved organic matter (DOM). As a consequence, dissolved organic matter will be reduced, and hence, reduction of dissolved metals.

Regarding the influence of organic matter on heavy metal mobility, different opinions have been expressed by researchers. For example, Tessier *et al*. (1996*),* Christensen (1998), and Calmano *et al*. (1993) mention that in the case of low pH conditions organic matter decreases the mobility of heavy metals. On the other hand, Redman *et al.* (2002) and Sauve *et al*. (2000) confirm that the mobility of heavy metals increases with increasing organic matter content. In addition, increased application of organic matter to the soil will affect the mobility and bioavailability of heavy metals, as this changes the soil pH and cation exchange capacity; therefore, the solubility of metals and their bioavailability will be changed as well (Narwal and Singh, 1998; Weber and Karczewska 2004). Humic acids have functional groups that give them a negatively charged surface, so when they are in solution they increase

the mobility of heavy metals (Shen, 1999). The large proportion of organic matter in sediment is thought to be found as a coating on the particle surface; this is likely to be due to the absorption of organic matter on iron oxides (Tessier *et al.,* 1996*).* Kashem and Singh (2001a) conducted a study in which they found that in soil treated with organic matter the solubility of Ni, Cd, and Zn was 2-5 times less than in unamended soil. This is likely to be due to the formation of complexes with organic matter, which prevent the mobilisation of the metals mentioned above. Another important relationship between organic matter and trace elements has been found by Yaru *et al*. (1999). They found a negative correlation between the Cu content of plant and organic matter and this was attributed to the binding of Cu to organic matter, which makes it less available to plants. As a result, the organic material content of soil could control the uptake amount of some heavy metals. Kashem and Singh (2001b) carried out a study to examine how the uptake of Cd, Ni and Zn in three types of soils changed when 4% organic material was added. These authors found that the total plant uptake of Cd decreased by 30%, and that of Ni decreased by 37%. By contrast, Zn uptake did not show any remarkable change when extra organic material was added. Finally, it should be mentioned that both the organic matter amount and the source of organic matter affect the species of metals and their uptake in soils (Narwal and Singh, 1998). For instance, the concentration of Cd, Ni, Cu, and Zn in wheat from cow manure treated soil is different from that from pig manure treated soil (Narwal and Singh, 1998).

Overall, the determination of organic matter content in soil contamination studies is very important as it represents the key sorbents of heavy metals. Therefore, many methods have been suggested to find the concentration of organic matter. The loss of ignition method can be used for this purpose, and In this method, samples are

ignited to a temperature of 375^{o}C, and the difference in weight before and after ignition represents the amount of organic matter (Radojevic and Bashkin, 2006).

5.2.2. Soil pH

The concentration of hydrogen ions in the pore space solution between the particles of soil is called pH; it is in balance with the surrounding negatively charged particles (Alloway, 1995). Many researchers (e.g. Esnaola and Millan (1998) and Chuan *et al*. (1996)) have pointed out that pH is the significant agent that controls heavy metals' mobility. In soil, the balance state between basic cations, such as Ca^{+2}, Mg^{+2}, K^{+1}, Na^{+1}, and heavy metal cations, as well as negatively charged organic matter and clays, is the main factor on which the acidity or alkalinity of the solution depends (Troeh and Thompson, 1993).

The hydrogen ion (H^{+}) has a strong affinity to negatively charged surfaces and displaces most other cations; hence it plays an important role in binding metals to the surface of clay minerals and organic materials (Alloway, 1995). In addition, soil contamination probably affects the pH of soil because of the cation replacement process with the soil constituents. This is seen clearly in the case of lead and chromium than those of cadmium (Percival *et al.* 1999). This has been illustrated by Salam and Helmke (1998) and Fairhurst *et al.* (1995). As pH is increased, soil minerals (i.e. clays) lose protons and increase their negative charge, thereby, increasing the ability to attract heavy metals.

Different soil climates have different pH values. For example, in a humid climate, soils are usually acidic because of the leaching process (Ross, 1996a) and have a pH range of about 5-7 (Brady, 1984). In humid climates, due to the acidic conditions, as mentioned above, extra hydrogen ions will be added, which try to bind to the sites of negatively charged clay and organic matter; therefore, weakly bonded metals will

be released and consequently their concentration will be increased in the solution system (Brady, 1984). Furthermore, the pH range may indicate which form of metal can be absorbed. For instance, a study by Matera *et al.* (2003) found that arsenic (V) is absorbed to metal oxides in a pH range of 4-7, whilst arsenic (lll) is absorbed to metal oxides in a pH range of 7-10. As a result, the authors conclude that pH can be a selective factor for heavy metal absorption.

In acidic conditions, the majority of metals tend to be mobilised and accumulate strongly in alkaline conditions (Plant and Raiswell, 1983). For instance, Rending and Taylor (1989) found that higher concentrations of copper, zinc and nickel were soluble in acidic conditions compared with alkaline conditions. Various tests to measure heavy metal concentrations in different types of soils with different pH ranges have been conducted; the results support the above mentioned work. It was found that the concentrations of Zn, Cu, Cd, and to some extent Pb in pH conditions of 4-5 were greater than their concentrations in the pH range 5-7 (Smith, 1996). In the same context, Kashem and Singh (2001b) point out that in soil under low pH conditions, rice plants' uptake of cadmium, nickel and zinc is high; this is attributed to the fact that in such conditions these metals are more soluble and thus more available for plants. However, low concentrations of cadmium were registered by McBride (1980) in conditions of high pH as a consequence of binding cadmium to soil particles and making it less available to plants. It is also important to mention the effect of pH on the absorption of organic material to soil minerals and the consequent effect on the concentration of heavy metals in soils. Gu *et al.* (1995) point out that the absorption of organic matter to soil particles is reliant on pH, with a high tendency in low pH conditions. As a result, in such conditions high

concentrations of heavy metals are expected because metals will find more binding sites.

It is also crucial to mention the effect of pH on the bioavailability of heavy metals in soils. Different heavy metals behave differently with a change in soil pH, and this is clear in the total available amount for plant uptake (Smith, 1996). In addition, Kabata-Pendias (2001) found that the amounts of cadmium, nickel and zinc available for plant uptake are quite sensitive to soil pH changes, whilst copper, lead and chromium are less sensitive to the changes in soil pH. Furthermore, in low soil pH conditions (i.e. acidic condition) lead tends to be more bioavailable. The concentration of heavy metals in soil solution was investigated by Brujjer and Herms (1983), and they found that the concentrations of heavy metals with decreasing pH value increased in the following order: Cd > Zn » Cu > Pb.

5.2.3. Reduction-oxidation (redox) potential (Eh)

One of the most significant features of soil is the redox potential (Eh), which describes the relationship (balance state) between the oxidation and reduction for the soil system. It is usually measured in the unit of volts or millivolts (Calmano *et al.*, 1993). Rowell (1994) stated that redox potential has an important role in the mobility of heavy metals and represents an interesting factor for the determination of the possible release of heavy metals into soil and sediment environments. Oxidation and reduction have different meanings. In chemical terms, oxidation means loss of electrons, whilst reduction means gain of electrons (Calmano *et al*., 1993). It has been seen that in oxidised soil conditions, Eh values are between +300 mv and +800 mv, whereas in the case of reduced soil conditions, Eh values range between +118mv and -414mv (Bailey, 1980). Eh values can result in the acidification of soil and sediment systems. For instance, when reducing soil and sediment systems are

oxidised this is more likely to make the soil and sediment system acidified (Gambrell *et al*.1991, Christensen, 1998). Therefore, this system (as highlighted by Forstner (1993) and Gambrell *et al*. (1991) will be at the peak of acidification when the pH of the system has a range 2-3. As a result, this process is more likely to release heavy metals into the surrounding environment, especially in the case of oxidation of sulphide minerals (Jenkins *et al*., 2000.), as the following equation shows:

$$MS_{(s)} + 2O_2 \rightarrow M^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$$

Where: MS = sulphide minerals, M^{+2} = released element ion

Furthermore, the process mentioned above (acidification) is very important, especially with respect to iron sulphides and the sequential release of iron ions into the environment, in regard to what happens in acid- mine drainage affected areas. This can be illustrated by the following equations (Jenkins *et al*., 2000):

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 4Fe(OH)_3 + 8SO_4{}^{-2}{}_{(aq)} + 16H^+$$

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{+2}{}_{(aq)} + 4SO_4{}^{-2}{}_{(aq)} + 4H^+$$

$$4Fe^{+2}{}_{(aq)} + O_2 + 4H^+ \rightarrow 4Fe^{+3}{}_{(aq)} + 2H_2O$$

$$Fe^{+3}{}_{(aq)} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

In addition, as can be seen from some of the above equations, in some cases iron hydroxides are formed and these are well-known absorptive agents for potential toxic metals. Therefore, high levels of trace elements can be seen in areas where oxidation of sulphide minerals has occurred (Gambrell *et al.* 1991). This process (i.e. oxidised sulphide minerals) is likely to be of great interest in our study area (Ecton mining area) as this area has been mined for a long time, and high concentrations of

iron hydroxides-related trace elements are expected. Furthermore, the reduction-oxidation potential plays an important part in the transfer of contaminant metals, principally heavy elements and essential metals for organisms, such as N, P, and S (Radojevic and Bashkin, 1999). As a consequence, the amount of metals available to plants depends on whether the soil environment is oxidised or reduced. For example, some heavy metals (e.g. cadmium and zinc) are quite soluble in acidic soil and therefore are more available for plant uptake. However, these metals tend to be accumulated in the soil and less available to plants in reducing conditions (Plant and Raiswell, 1983; Kabata-Pendias, 2004). As a result, the redox potential governs the bioavailability of heavy metals in soils and sediments, and it can be seen from table 5.2 that different metals have different levels of bioavailability under different situations of reduction and oxidation (Kabata-Pendias, 2004).

Table 5.1: Bioavailability of elements in soil with different redox potentials condition (Source: Kabata-Pendias, 2004)

Soil condition		**Bioavailability**	
Redox	pH	Easy	Moderate
Oxidizing	< 3	Cd, Zn, Co, Cu, Ni	Mn, Hg, V
Oxidizing	>5	Cd, Zn	Mo, Se, Sr, Te, V
Oxidizing(Fe-rich)	>5	Non	Cd, Zn
Reducing	>5	Se, Mo	Cd, Zn, Cu, Mn, Pb, Sr
Reducing, with H_2S	>5	Non	Mn, Sr

It sould be noted that atmospheric factors, especially rainfall, affect soils' reduction and oxidation conditions, as mentioned by Kashem and Singh (2001 a). Kashem and Singh (2001a) found that a sixteen-week period of soil flooding minimised redox potential, increased pH and reduced solubility, exchangable portion and organic-bounded zinc and copper. In addition, the authors also point out that under the

conditions where the soil was covered with water, higher concentrations of oxidised and organic related fractions were found compared with non-flooded soils.

5.2.4. Grain size

One of the most important factors controlling the particle size of sediment is the precipitation conditions, and it is generally accepted that contaminants are related to smaller size particles (Singh *et al*., 1999). Therefore, grain size plays a significant role in relation to the accumulated concentrations of heavy metals on sediment surfaces. In this regard, clay minerals, which are a group of silicate materials with a particle size of less than 2μm, are very important (Rowell, 1994). Although clay minerals are the basic part of this group, humic materials, iron oxides, silicon dioxide, and calcium silicate might also be involved in it (Forstner *et al*., 2001). The smaller the grain size, the more surface area is expected; thereby high concentrations of heavy metals will be expected. For example, in a study carried out by Horowitz and Elrick (1987), they found that grain size, heavy metal concentration and surface area are associated with a strong correlation. In addition, Droppo and Jaskot (1995) point out that as fine particles have a large surface area compared with other sizes, grain size is a significant parameter for indicating the amount of metal associated with a particle surface. Furthermore, although the fine portion of sediments (i.e. clay size) has been mentioned as an important factor for finding pollutants, silt size is also considered as a factor to which high levels of accumulated metals can be attributed (Ackermann, 1980). Due to the presence of a large surface area in the case of clay and silt fractions, organic matter, which plays an important role in absorbing heavy metals, tends to be attracted and accumulate on the surface of the two sizes mentioned above (Cheshire *et al*., 2000). This probably explains why many researchers have found high levels of pollutant metals related to organic matter and

clay and silt fractions. For instance, Christensen (1998) states that high concentration of heavy metals was found to be associated with organic matter, clay, and silt fractions. However, heavy metals are also more likely to be associated with sand-sized sediments especially in the fluvial sediment system of areas with a long history of mining (Zhao, 2001). For this reason, mine workings in the United Kingdom were prohibited in many areas because of the risk that these activities might pose to the surrounding environment (Thornton, 1980). Moreover, it has been found that trace elements related to a coarser grain size, in fluvial systems, are accumulated in high concentrations in the upper attributes, whereas those associated with fine sizes are transported downstream for long distances (Lewin and Macklin, 1987). Overall, it is very important to consider sediment particle size, especially clay and silt sizes, in environmental pollution studies, as they represent a key factor in attracting contaminating metals.

5.3. Techniques of estimating heavy metals bioavailability

Nowadays much consideration is given to the pollution caused by potentially toxic metals and their adverse effects on the ecological system and human health. As a result, lots of studies have been performed to investigate and measure these constituents, as they have the ability to accumulate in the upper layer of the soil profile, posing environmental risks to the surrounding area (Weber and Karczewska, 2004). Therefore, indicating and measuring the bioavailable amount is very important, as it will help enable a better understanding and estimation of the risk that heavy metals can pose to living organisms. To this end, different researchers have used different chemical reagents to extract the bioavailable fractions because a particular reagent might be suitable to extract a specific pollutant in some areas but might not be appropriate for the same metals in a different location (Davis, 1983). To

predict and simulate the bioavailable fraction of heavy metals in soil and sediments, investigators have used a wide range of extractants including mineral acids such as 1 N HCl, buffer solutions, for example 1 M NH_4OAc, salt solutions, for instance 0.1 M $CaCl_2$, and chelating agents, such as EDTA (which was used in this study) and DTPA (Adriano *et al*., 2004). According to MAFF (1986) and Gleyzes *et al*. (2002), using Ethylene Diamine Tetra Acetic Acid (EDTA), which is considered to be bioavailable to plants, in a one-step extraction, it is possible to extract exchangeable metals, soluble metals and some metals bound to carbonate and organic matter. In addition, EDTA, according to McGrath and Loveland (1992), has been used in England and Wales (Table 5.2) to extract the bioavailable fractions of some studied heavy metals in soils.

Table 5.2: Summary statistic of some selected heavy metals extracted by EDTA from topsoil in England and Wales (n=5679). (adopted from McGrath and Loveland, 1992).

Elements	Min	Max	Mean	Median	Skewness	Kurtosis	CV%
Cu	0.3	431	6.4	4.6	18	514.4	172
Pb	1.2	6057	27.8	13.3	32.8	1386	430
Zn	0.5	712	9.7	5.3	16.6	368.6	254
Mn	<0.02	3108	159.5	110	4.6	39.3	118
Ni	<0.2	73	1.6	1.1	13.9	384.6	122
Cd	<0.1	18	0.3	0.2	16.7	411.7	162

CV% is the coefficient of variation = S.D/Mean%

During the daily life of plants, they usually absorb all of their required materials via their roots from the soil solution, without considering whether the absorbed metals are harmful or not, and this changes the soil content of different metals. For example, Hamon et al. (1997) point out that metals in soil solution are in an equilibrium state with the exchangeable phase, which is linked to the surface of grain

particles and the fraction absorbed by functional groups of organic matter. As a result, plants will contribute to changing the physical criteria of the soil surrounding them, and thereby influence the bioavailability of heavy metals in the soils (Alloway, 1995). Consequently, due to the disturbance of the equilibrium state, metals are very likely to be released into the soil from other fractions and some of these might become available to plants that were not present before (Grinsted *et al.,* 1982). In addition, natural processes such weathering can change the form of metals in the soil and thus affect their mobility and bioavailability. Moreover, there are many factors (refer to section 5.2) that play a significant role in changing the chemical form of heavy metals in soil, and thereby change their bioavailability capacity in soil (Hamon *et al.,* 1997).

Figure 5.1: View of study area showing the topography of the area with grazing cattle

In this chapter the bioavailability of heavy metals to plants will be considered and estimated because the majority of the study area at the present time is used for stock rearing and pastures for grazing animals (Fig. 5.1). As a result, heavy metals are very likely to be transferred to human beings via plants and animal products. According to Mench and Martin (1991), potentially toxic metals, such as Cu, Pb, Ni,

Cd, Co and Hg, after being taken up by plants, move directly to the human body when they eat plants or are taken up by the animals grazing on the land. In addition, in areas with a long mining history such as the current study area, large amounts of heavy metals (e.g. Cd, Pb) could be transferred to animals' bodies via the ingestion of fine soil containing harmful metals when they are grazing on the grass. This will be a significant pathway i.e. soil-grass-animal, by which metals are entering grazing animals and thereby the human body (ICRCL, 1990). Therefore, measuring the bioavailable fraction of heavy metals is crucial when appraising pollution and risk assessment (Adriano *et al.,* 2004). To this end, the bioavailable fraction of heavy metals can be estimated using different methods, as described below.

5.3.1. Metals accumulation index

By this method, the bioavailability of heavy metals to plants can be calculated using the percentage of heavy element concentration in plants to the total concentration of heavy metals in soils, as the following formula (Kashem and Sigh, 2001):

Accumulation index = (Metal concentration in plant / Total metal concentration in soil) ×100

This index has also been called the concentration ratio (CR) by Bunzl *et al.* (2001), due to the use of the percentage of metal concentration. It should be noted that this index gives a reliable indicator of the bioavailable amount of heavy metals to plants because it uses the actual available amount of the pollutants that have been taken up by plants and shows better quantitative data about the available amount of metals to plant in soils. Kashem and Singh (2001a) point out that the accumulation index appears to have higher values in soils affected by human activity than in soils with a natural metal amount.

5.3.2. Bioavailable ratio

In the current study this method was used to measure the bioavailable fraction of heavy metals to plants for the collected samples. This approach gives the ratio of the bioavailable fraction of heavy metals to plant to the total amount of metal in the soil, which is calculated using the following equation (Kashem and Sigh, 2002a; Sanchez *et al*., 1999):

Bioavailable Ratio = (Bioavailable metal fraction / Total metal concentration in soil) × 100

This method depends on the amount of the bioavailable fraction of the heavy metal to plants in soil, which is measured using chemical reagents (EDTA), as mentioned before (refer to chap. 3 for methodology).

5.4. Bioavailability of heavy metals in collected soil and floodplain samples

The bioavailable fraction of the selected heavy metals for the collected soil and floodplain samples was measured using a one-step extraction with 0.01 M EDTA. Summary statistics of the findings are shown in table (5.3), and all of the data results are presented in appendices (E and F).

From table 5.3, it can be seen that the bioavailable fraction for all of the metals varies between different sample types. For instance, the EDTA amount for Cu ranged from 9.07 mg/kg to 22.65 mg/kg for the floodplain and soil samples, respectively. The EDTA extractable for all of the metals was lowest in the floodplain samples. However, the soil samples had the largest EDTA extractable amount for all of the metals, except Mn and Cr in the floodplain samples (Table 5.3).

Cu, Pb, and Zn, as has been previously mentioned, were extracted extensively from sulphide ores during the mining operations from Ecton Hill (refer to chap.2, mining history section). As a result, the highest levels of EDTA extractable for these metals in the soil samples are more likely attributed to the former mining activities in the

area. The bioavailable amount for the collected samples was found to have the following order:

Soil samples > floodplain samples.

5.4.1. Assessment of EDTA extracted metals in the area on the basis of national mean amounts

As mentioned earlier, all of the collected samples were analysed for their bioavailable fractions of the metals being studied (Cu, Pb, Zn, Mn, Cr, Ni, and V) using a 0.05M EDTA solution at pH 7; the summary statistics are available in appendices (E and F).

Table 5.3: Showing the summary statistics of the bioavailable fraction of the selected heavy metals (mg/kg) in the collected soil and floodplain samples.

All sample types	**Cu**	**Pb**	**Zn**	**Mn**	**Cr**	**Ni**	**V**
Soil samples (n=37)							
Max	188.86	2244.40	634.07	238.88	0.22	2.15	0.94
Min	0.81	1.58	0.82	4.29	0.02	0.14	0.03
Average	22.65	207.58	104.01	67.65	0.08	0.82	0.18
SD	42.36	453.42	169.04	59.71	0.05	0.56	0.19
Bioavailable Ratio (%)	3.81	6.53	4.49	6.30	0.22	2.15	0.47
Floodplain samples (n=11)							
Max	23.45	31.80	80.79	117.55	0.13	1.11	0.22
Min	2.37	4.30	6.22	35.90	0.05	0.66	0.01
Average	9.07	14.32	20.24	79.82	0.09	0.86	0.06
SD	5.27	6.88	21.66	23.74	0.02	0.16	0.06
Bioavailable Ratio (%)	6.77	6.36	5.09	7.57	0.19	2.35	0.18

It is very important to know and appraise how high the extracted levels are by comparing the calculated amounts with the national average levels, which are listed in table 5.2. These levels have been adopted from McGrath and Loveland (1992), who point out that the EDTA extraction amounts of the metals mentioned in table 5.2 in England and Wales have been measured and displayed in mg/kg of dried soil

sample. The bioavailable fractions (i.e. ETDA metal extraction) of the selected metals in all of the collected samples were compared with the national mean values for England and Wales (McGrath and Loveland, 1992), and results are shown in (Table 5.4).

Table 5.4: Showing amount of EDTA metal extracted in collected samples compared to the national average amounts of England and Wales (adopted from McGrath and Loveland, 1992)

Sample types	**Cu**	**Pb**	**Zn**	**Mn**	**Cr**	**Ni**	**V**
Soil samples (n=37)	3.53	7.47	10.72	0.42	n.a	0.52	n.a
Floodplain samples (n=11)	1.30	0.49	1.65	0.50	n.a	0.53	n.a
National average values	6.4	27.8	9.7	159.5	n.a	1.6	n.a

From this table, the focus will be on Cu, Pb, and Zn because these metals were extracted from the study area for a long time (refer to mining history in chap 2). From table 5.4, it can be seen that the amount of EDTA metal extractable for all of the selected metals from the soil samples exceeded the national average amounts for England and Wales, except for Mn and Ni. The EDTA values for Cu, Pb, and Zn (3.53, 7.47, and 10.72, respectively) in the soil samples were 3.53, 7.47, and 10.72 times the national average amounts of England and Wales. However, with regard to the floodplain samples, all of the EDTA metals extractions were lower than the national mean levels, except for Cu and Zn for the floodplain samples.

When the area was explored during sampling, the majority of it was found to be used for cattle rearing and crop production. As a result, the high EDTA metal extraction in soils from the area could indicate a high risk to animals and human beings through the soil-plant-animal- human body exposure pathway. According to Archer and Hodgson (1987) and ICRCL (1990), Cu, Zn, and Ni have a toxic threshold EDTA

value of 70mg/l, 130mg/l, and 20mg/l, respectively. Above these limits, the bioavailable fractions of these metals will have toxic effects on the grazing animals, and thereby adversely influence humans. Therefore, based on the above guidelines for Cu, Zn, and Ni and the calculated EDTA trace element extractions for each sample (see appendix E for EDTA metal amount for individual samples) all of the locations from which the samples were collected are safe with respect to toxicity, except samples ES6, ES7, ES8, ES9, ES26, ES32, and ES37 in regard to Zn, and ES9, ES9, ES32, and ES37 in regard to Cu. The possible source of such levels is more likely to be anthropogenic than natural enrichment because, as mentioned previously, the area was mined for sulphide minerals for a long period (refer to mining history in chap. 2).

5.5. Relationship between EDTA metal extractions (i.e. Bioavailable fraction) and the total amount of metal concentration

Although the total concentration of heavy metals in soils is very significant as it gives information regarding the degree of contamination in the soil of interest (Li, and Thornton, 2001), it does not give information about heavy metal speciation and bioavailability, and hence, it only provides limited knowledge about the effects of potentially toxic metals on living organisms (Tessier *et al*., 1979). Therefore, measuring the bioavailability of heavy metals is more important when studying their consequences for the surrounding environment. To this end, all of the collected soil and floodplain samples were extracted for their bioavailable amount of heavy metals using a 0.05 M EDTA solution, pH 7 (refer to chap. 3 for procedure used).

The relationship between this fraction and the total concentration was investigated because such a correlation may provide useful information regarding whether there

is any link between the two levels. The relationship between the EDTA metals in the studied samples and the total concentration is shown in table 5.5.

Table 5.5: Correlation coefficient between EDTA metal extraction and the total concentration in collected soil and floodplain samples in Ecton mining area.

All samples	**Cu**	**Pb**	**Zn**	**Mn**	**Cr**	**Ni**	**V**
Soil samples (N=37)	0.763**	0.946**	0.917**	0.840**	0.035	0.408*	0.097
Floodplain samples (N=11)	0.823**	0.549	0.99**	0.862**	-0.141	-0.168	0.289

**: correlation is significant at 0.01 levels (2 tailed)
*: correlation is significant at 0.05 levels (2 tailed)

From Table 5.5, based on the correlation coefficient (r) and level of significance, it can be seen that a strong positive correlation was found between the EDTA metal fractions and their total concentrations for Cu, Pb, Zn and Mn for both soil and floodplain sample, except for Pb in the floodplain samples. According to McGrath and Loveland (1992), strong correlations between the EDTA for Cu, Pb, Zn and Mn and their total concentrations were also found in England and Wales, with the EDTA Ni fraction being linked weakly with the total concentration. In addition, a strong positive correlation for Cu, Pb, Zn, and Mn was also reported by Hernandez and Pastor (2008) in Sierra de Guadarrama in Spain, for an area with former mining activities. However, a strong negative correlation was found between the EDTA Cr fraction and its total concentration (Table 5.5). This might be attributed to the low solubility of Cr in soil (Alloway, 1995), and hence, less is available for plants. Regarding the correlation between the EDTA V fraction and the total amount, it is clear that this element displays a weak correlation. A possible explanation for such relation might be attributed to the fact that this element, as pointed out by Cheshire *et al,* (1977), has a strong association with humic and fulvic acid in soil, which makes

it less extractable and thus less available to plants. As a result, a weak link between the available and total concentrations will be expected.

Overall, focusing on the metals Cu, Pb, and Zn, which were extensively mined from the study area (refer to mineralization section in chap. 2), it is worth noting that a positive correlation between the EDTA metal fractions and the total amount may suggest that the EDTA fractions will increase with increasing total amount. In another words, an elevated total amount will probably lead to a high bioavailability amount. Such a relation has been recorded elsewhere. For example, Yaru and Buckney (2002) found that all of the metal extractions from sequential extraction in soils from Papua New Guinea were correlated strongly with the total Cu amount.

5.6. Relationship between bioavailable fraction and organic matter content, pH and different grain size fractions using Principal component analysis (PCA) approach

The key point of principle component analysis (PCA) is to eliminate the dimensional space of original datasets to new subsets of the variable of interest (Einax *et al.,* 1997). In this method of analysis, raw data have to be converted to principal components via eigenvalues by which the variance of extracted components are decreased on the basis of significance. To this end, in the current study the principal component analysis (PCA) approach was applied to find the possible associations between the bioavailable fractions of studied heavy metals and the physico-chemical properties of the soils (i.e. organic matter contents, pH value, and different granulometric data). Principal component analysis (PCA) results for both soil types (i.e. topsoils and floodplain samples), along with the Eigenvalues and total variance explained are shown in the Tables 5.6, 5.7).

In the case of soil samples, 4 principle components have been extracted which represent 70% of the total variance (Table 5.6). Results show that the first factor (F1) is mainly associated with the silt and clay fractions, with a positive relation with soil pH, bioavailable fractions of Zn, Ni, and V. This may indicate that fine particles (i.e. clay and silt), and pH are controlling the bioavailable fractions of these metals. According to Brady (1984), the soil pH values in humid areas are ranged between 5 - 7, which is similar to that of the current study in which the pH values for the majority of collected samples are below 7. As a result, such condition would provide more hydrogen ions (H^+) to be available for competing metal cations for the binding sites on the clay and organic matter, resulting release metal ions, and thus high concentration of metals could be available for plant uptake. However, the second factor (F2) was strongly associated with the EDTA extractable amount of Mn, Cr, Ni, and organic matter contents. Such association is more likely to indicate that the extractable amounts of the aforementioned metals are governed by organic matter contents which play a significant role for metal binding. Shuman et al. (2002) highlighted that, high amount of organic matter increases both the surface area and binding sites for metal absorption. As a consequence, high concentrations of metals would be available as bioavailable fraction. The third factor (F3) is mostly connecting the bioavailable fraction of Cu, Zn with the soil pH and organic matter contents, indicating that these two parameters are more likely driving the extractable amounts of both Cu and Zn. Bioavailable fractions of metals such as Pb, Zn, and V are correlated with the organic matter contents in the fourth Factor (F4), with approximately similar factor loading for Pb and V. such association, similar to the case of F4, may seem to indicate that organic matter contents control the bioavailable portion of these elements.

However, regarding the floodplain soils, four principal factors were extracted (Table 5. 7), which illustrate 96.65% of the total variance. The strongest association of the data is explained by the first factor (F1), which describes the majority of the variance (65.48), and correlated mostly with the bioavailable fraction of all metals studied (i.e. Cu, Pb, Zn, Mn, Cr, Ni and V, organic matter contents and soil pH, clay and silt fractions. This might indicate that these components are acting a significant role for controlling the bioavailable amounts of these metals, and especially in the case of clay and silt, which provide bigger surface area for absorption, thereby; high concentrations of these metals are expected, resulting in high bioavailability.

Table 5.6: Principal component analysis and factor loading for collected soil samples

Rotated Component Matrix[a]				
	Components			
	1	**2**	**3**	**4**
Cu_bio	-.220	-.121	.795	.001
Pb_bio	-.024	-.210	.099	.865
Zn_bio	.053	-.275	.753	.362
Mn_bio	-.094	.933	-.164	-.039
Cr_bio	-.061	.934	-.101	.141
Ni_bio	.151	.601	-.021	-.248
V_bio	.061	.067	.153	.876
pH_value	.142	-.089	.550	-.010
Organic_M%	-.058	.220	.521	.342
clay	.895	-.105	-.046	-.029
silt	.858	.057	-.113	-.044
sand	-.846	-.043	-.154	-.098
Eigen Values	2.955	2.382	1.950	1.137
% of Variance	24.623	19.854	16.250	9.476
Cumulative %	24.623	44.477	60.726	70.202

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 5 iterations.

With regards to component 2 (F2), the bioavailable fractions of Cu, Pb and Zn are associated with this component although the relationship is weaker than those of F1. However, this component (F2) is also containing sand being correlated with a fairly strong and positive correlation (0.744). This seems to indicate that sand governs the bioavailable amount of these metals to some extent. The best explanation of such association is that mining waste-related heavy metals have been dumped in the River Manifold during mining process. Subsequently, these sediments have been moved downstream and deposited in the River floodplain resulting in high levels of metal to be recorded, hence high bioavailability. However, in the case of factors F3 and F4, these two factors did not show any link with the bioavailable amount of the metals under study, except with Ni (0.72) and Mn (0.42), which do not demonstrate any correlation with any of the soil specific factor (i.e. organic matter, soil pH, clay and silt fractions.

It can be concluded that, PCA analysis has shown different association forms between the bioavailable fractions of studied heavy metals and soil specific parameters (i.e. pH, organic matter amounts, and different particle size range). However, the effect of these parameters are various among different soil types, with predominant influence of the organic matter content in the case of floodplain sample, and clay and silt fractions in terms of soil samples (Tables 5.6 and 5.7).

5.7. Summary

Bioavailable fractions (i.e. EDTA metals extraction) for the metals studied were assessed by comparing them with the national mean values for England and Wales. Findings demonstrate that the amount of EDTA metal extractable for all of the selected metals from the soil samples exceeded the national average for England and Wales, except for Mn and Ni.

Table 5.7: Principal component analysis and factor loading for collected floodplain samples

Rotated Component Matrix[a]				
	Components			
	1	**2**	**3**	**4**
Cu_bio	.900	.377	-.097	-.039
Pb_bio	.872	.368	-.130	.166
Zn_bio	.893	.361	-.189	-.144
Mn_bio	.850	-.262	.419	.142
Cr_bio	.931	-.196	.263	.063
Ni_bio	.639	.179	.717	-.038
V_bio	.941	.268	-.174	-.035
pH_value	.750	.425	-.319	.173
Organic_M%	.933	.033	.042	-.321
clay	.642	-.700	-.137	.243
silt	.699	-.652	-.204	.145
sand	-.522	.744	.184	.366
Eigen Values	7.857	2.269	1.049	0.424
% of Variance	65.478	18.906	8.739	3.532
Cumulative %	65.478	84.384	93.123	96.65

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
a. Rotation converged in 5 iterations.

The EDTA values of Cu, Pb, and Zn in soil samples were 3.35, 7.47, and 10.72 times the national average amount, respectively. However, the bioavailable fractions for the floodplain samples were lower than the national mean values; except for Cu and Zn.

The relationship between the bioavailable fractions and the total heavy metals was examined; the results indicate that there is a positive correlation between the EDTA metal fractions and their total concentrations for Cu, Pb, and Mn for all of the sample types, except for Pb and Mn in the floodplain samples. Such positive correlation

between the total and the bioavailable may suggest that an elevated total amount probably result in a high bioavailable amount to be recorded.

Principle component analysis (PCA) approach was applied to find the possible associations between the bioavailable fractions of the examined heavy metals and the physico-chemical properties of the soil (i.e. organic matter content, pH values, and different granulometric classes. From the analysis, four components were extracted, which explain 70% of the total variance. The results show that there are different association forms between the bioavailable fractions of the metals studied and soil specific parameters among the different soil types, with the predominant influence of clay and silt fractions in the case of the stream sediment samples, for which the clay and silt size range shows a strong association with the bioavailable amounts of the extracted metals.

Chapter Six: Amounts, distribution mode, and correlation of selected heavy metals in floodplain samples from the Ecton mining area.

6.1. Introduction

In chapter four, the spatial distributions and contamination assessment of the heavy metals present in the collected soil samples were illustrated. Then, in chapter five, the bioavailability of the studied metals in all of the samples was evaluated. Consequently, it would be very useful to evaluate the amounts, distribution and possible association between the studied heavy metals in the floodplain samples of the River Manifold.

6.2. Heavy metals sources

In nature, heavy metals have different sources. Alloway (1995) highlighted that floodplain soils are an open media for heavy metals to inter from different sources as soils are considered to be the intermediate region between the atmosphere and the earth's surface. However, pollutants in the soil are more likely to have come from both sources, anthropogenic and natural (Weber and Karczewska, 2004).

6.2.1. Natural sources of heavy metals

According to McGrath and Loveland (1992), the major source of heavy metals in soils is the weathering process of the parent rocks from which the soils are formed. Therefore, settled soil that is created from original rocks (i.e. parent rocks) without changing usually reflects the chemical composition of the parent rocks (McGrath and Loveland, 1992). Regarding the composition of the earth's crust, Davies (1980) points out that igneous and metamorphic rocks form about 95% of the earth's crust with the rest being sedimentary rocks. Furthermore, the author also mentions that sedimentary rocks are the main source of heavy metals because they cover about

75% of the earth's surface, and shale itself comprises about 80% of sedimentary rocks. It has been found that parent rocks contribute different amounts of heavy metals to soils under different conditions. For instance, sulphide minerals form just a small part of the crust's composition and under normal conditions they contribute a small amount of heavy metals to soil. In mining areas, however, the concentration of heavy metals is high in the soils around (Davies, 1983). In addition, in nature, minerals are found to contain impurities of other metals. Table 6.1 illustrates the most common metals that have been found to be associated with sulphide minerals.

Table 6.1: Some selected sulphide minerals with associated heavy metals (adopted from Davies, 1980).

Minerals	**Associated heavy metals**
Sphalerite (ZnS)	Ag, Au, Ba, Cd, Co, Cu, Ga, Ge, Hg, In, Sb, Sn
Galena (PbS)	Ag, As, Au, Ba, Bi, Cr, Hg, Ni, Sb, Sn, Te, Ti, Zn
Chalcopyrite ($CuFeS_2$)	Ag, Co, Ge, In, Mn, Ni, Se, Sn
Pyrite/ Marcasite (FeS_2)	Ag, As, Au, Co, Cu, Ni, Pb, Ti, 5Tl
Arsenopyrite (FeAsS)	Co, Ni, Mn

Moreover, the author also points out that shale and sandstone are the main sedimentary rocks, with sandstone being formed from sand- size grains and contributing less heavy metals. However, shale, which is recognised by its black and dark colour due to the large amount of sulphide minerals and organic matter it contains, has high levels of U, Cu, Pb, Zn, Cd, Au, V, Mo and just a small outcrop of it in the area can make unusual metal levels (Davies, 1983; Ross, 1996b). Limestone is well known to have only small amounts of heavy metals and plays a significant role in balancing the pH condition of soils due to its alkaline nature. It can be utilised to increase the pH (Li, 1993). It should be noted that under normal conditions, soils

usually contain a low concentration of heavy metals, with the exception of soils produced from shale (Jackson and Alloway, 1991), and the best example of a natural abundance of heavy metals in soil is the high levels of Cr and Ni in soils derived from serpentine (Weber and Karczewska, 2004). The mean concentrations of some selected metals in several rocks and soils, and in the Earth's crust are shown in Table 6.2 (Levinson, 1974). According to the author, some rocks display differences in regard to their abundance of heavy metals because the heavy metal content is controlled by the diversity of the chemical composition of the source and the physical and chemical processes by which the rocks were formed.

Table 6.2: Mean abundance of selected metals in the Earth crust, soil and rocks (mg/kg) (adopted from Levinson, 1974).

Elements	**Earth's crust**	**Ultra-basic**	**Basalt**	**Granodiorite**	**Granite**	**Sandstone**	**Shale**	**Limestone**	**soil**
As	1.8	1	2	2	1.5	1	15	2.5	1.50
Cd	0.2	-	0.2	0.2	0.2	-	0.2	0.1	1
Co	25	150	50	10	1	0.3	20	4	1-40
Cr	100	2000	200	20	4	35	100	10	5-1000
Cu	55	10	100	30	10	-	50	15	2-100
Hg	0.08	-	0.08	0.08	0.08	0.03	0.5	0.05	0.03
Mn	950	1300	2200	1200	500	-	850	1100	850
Mo	1.5	0.3	1	1	2	0.2	3	1	2
Ni	75	200	150	20	0.5	2	70	12	5-500
Pb	12.5	0.1	5	15	20	7	20	8	2-200
Zn	70	50	100	60	40	16	100	25	20

6.2.2. Anthropogenic sources of heavy metals

The second main source of heavy metals in soils is related to human activities, for example industrial operations of materials, including solids and fluids are added to the land or dumped like waste materials, mining and smelting of mineral ores, the application of materials in agriculture such as fertilisers, animal manure and sewage sludge (Nicolson *et al*., 2003; MAFF, 1993). One of the most important anthropogenic sources that release high amounts of heavy metals into soils is mining activities, such as those that happened during the 19th and early 20th centuries in the UK, as a consequence of insufficient ore separation during mining processes (Alloway, 1995). In addition, such a high input of heavy metals into soil during that period was due to the absence of specific statutory laws in the UK dealing with the disposal of mining waste (Davies, 1983). Consequently, elevated concentrations of metals have been found in areas around former mining locations (ICRCL, 1990). The best example of that is our study area where high levels of Cu, Pb, and Zn have been detected (refer to chapter 3).

In the UK, metals have been extracted from different ore fields and each has specific related metals. Table 6.3 lists various mining areas from which different metals have been extracted.

Table 6.3: The main ore fields with different associated metals in the UK.

Ore fields	**The major associated metals**
North Pennines	Pb, Zn, F, Cd, Ba*
Lake district	Cu, Pb, Zn, W*
South Pennines	Pb, Zn, F, Cu, Cd, Ag*
North Wales	Pb, Zn, Cu, Cd, Ba*, Au*
Central Wales	Pb, Zn
Mendips	Pb, Zn, Cd
Cornwall and Devon	Cu, Pb, Zn, Sn*, Ag*, W*
West Shropshire	Pb, Zn

[*] metals are rated not to be a problem for agriculture

Although mining is a major anthropogenic source of heavy metals in soil, other sources cannot be ruled out. For instance, a huge amount of refuse materials, such as sewage sludge, which contains high concentrations of metals, have been added to agricultural land in order to increase crop production. According to Nicholson et al. (2003), a survey was performed in 1996 and 1997 regarding the amount of sewage sludge used in agriculture. This study showed that nearly 50% of the total sewage sludge produced was added to agricultural land in England and Wales. As a result, a large amount of heavy metals have been added to the soils. To eliminate the adverse effects of adding the sludge to agricultural soils, the government set out a law to control the quality of sludge added to soil in England, Wales, and Scotland, and put the responsibility on farmers to follow and meet the appropriate quality standards for additive sludge (Environmental agency, 2006b). Furthermore, the application of materials, such as phosphate fertilisers, pesticides and lime can cause an increase in some heavy metals, for example Cd, Zn, and Cu, in particular when phosphate fertilisers are applied continually (Alloway, 1995; Nicholson *et al.,* 2003). Moreover, Alloway (1995) points out that the manure of hens and pigs contains high levels of Cu and Zn. This has been added to plants for health reasons, but it may lead to increased levels of these elements when added to the soil. In addition, agricultural materials such as fertilisers usually contain heavy metals in tiny concentrations. If the basic material were to be modified during production that would help to reduce the amount of heavy metals added to the soil. Nicholson *et al.* (2003) conducted a study to determine the major sources of heavy metals and their amounts in agricultural soils during the year 2002 in England and Wales. They found that the key sources are sewage sludge, atmospheric deposition, inorganic fertilisers, lime, cattle manure, industrial by product waste, and irrigation waters.

Among these sources, atmospheric deposition of heavy metals, which comprises power plants, mining processes and waste burning, is considered to be the major source of heavy metals in soil, with the output comprising 25% - 85% of the total output (Nicholson *et al.,* 2003; MAFF, 1993).

Table 6.4: The annual input of heavy metals (t) from various sources to agricultural soils during the year 2002 in England and Wales (adopted from Nicholson et al., 2003).

Sources	**Zn**	**Cu**	**Ni**	**Pb**	**Cd**	**Cr**	**As**	**Hg**
Atmospheric deposition	2457	631	178	604	21	83	35	11
Livestock manure	1858	643	53	48	4.2	36	16	0.3
Sewage sludge	385	271	28	106	1.6	78	2.9	1.1
Industrial wastes	45	13	3	3	0.9	3.9	nd	0.21
fertilizers	266	53	37	16	12	126	8.5	0.1
agrochemicals	21	8	0	0	0	0	0	0
Irrigation waters	5	2	<1	<1	<0.1	<1	<0.1	nd
Composts	<1	<1	<1	<1	<0.1	<1	nd	<0.1
Total	5038	1621	299	778	40	327	62	13

[nd]: no data

From Table 6.4, it can be seen that the contribution of Zn from different sources to agricultural soils was the highest, followed by copper and lead. Such findings suggest that agricultural lands in England and Wales have big hazards in terms of contamination with potentially toxic metals. It is worth noting that although flood events were not taken into account in the total output of heavy metals into agricultural soils in England and Wales, because it was difficult to evaluate their contribution to the total output, floods play a significant role in transferring and carrying stream-sediment associated heavy metals and depositing them downstream. Finally, having reviewed both natural and anthropogenic sources of heavy metals, it would be useful to find data regarding the contribution of each to the

environment. To this end, Nriague (1990) highlighted that globally, since 1900, the contribution of anthropogenic sources of heavy metals to the environment has been larger than that of natural sources (Table 6.5).

Table 6.5: Average ratio of anthropogenic / natural sources emission of heavy metals in terms of global scale since 1900 (adopted from Nriague, 1990).

Heavy metals	Anthropogenic/natural emission ratio	Globally increase emission rate since 1900 (%)
Cd	5.85	8
Ni	1.86	51
Zn	2.3	8
Pb	27.67	9
Cu	0.85	6

From Table 6.5, it can be observed that since 1900, Cd, Zn, and Cu become 5.85, 2.3, and 27.67 times, respectively, more than the natural input that have been released to environment. As a result, human activities have a significant role in the presence of high levels of potentially toxic metals in soils all over the world.

6.3. Heavy metals within floodplain soils, pollution and accumulation

According to Alloway (1995), various studies of heavy metal concentration in areas with a high population, mining areas, and main road networks, have shown that such areas have soils that contain elevated amounts of lead, cadmium, mercury, and arsenic from different sources. However, in riverine systems, pollutants of trace elements, agrochemicals such as fertilisers, and pesticides, are found to be related to a specific grain size (Alexander and Marriott, 1999). This is to say that different grain sizes have various concentrations of heavy metals. In addition, in floodplain soils, although high concentrations of heavy metals have been found to be associated with fine grain size soils, such concentrations may be related to sand size, especially in the upper courses of river, where high human activities such as

mining operations have been carried out (Zhao, 2001). As a result, Thornton (1980) pointed out that while the mining activities in the UK were restricted and stopped for a long period, due to these activities huge areas have been found to be contaminated. For example, the floodplain soils of mid-Wales have been investigated by Abraham and Steigmajer (2003), who found that these soils contain high concentrations of lead, copper, cadmium and zinc. Such high concentrations were attributed to the past mining activities in the area. Among these contaminants, lead had the highest concentration, which ranged from 240 mg/kg to 2940 mg/kg, 105 mg/kg to 1218 mg/kg, 46 mg/kg to 1554 mg/kg, and 122 mg/kg to 2142 mg/kg in the Rivers Clarach, Rheidol, Teifi, and Ystwyth, respectively. According to the author, the highest concentration of lead (i.e. 2940 mg/kg) was 50 times more than that found in the Aeron valley. Furthermore, Zhao (2001) reported that extensively elevated concentrations of lead, cadmium, and zinc (30.1-6809 mg/kg, 0.2-7mg/kg, and 44.5-984.6 mg/kg) were recorded in the floodplain soils of the River Cerist in the middle of Wales. Such floodplains are considered to be highly polluted with the mentioned metals, and higher as 141.6 times as the geochemical background of Pb. In the UK, floodplain soils are usually used for agriculture and livestock rearing and our study area is a good example of such usage (as seen during field investigation). Therefore, evaluating floodplain soil polluted with heavy metals is very important and has been achieved in many places. For instance, the floodplain soils of the Tamar Valley in the UK were evaluated by Thornton (1980), who found that the soils were extremely contaminated with a high concentration of arsenic, copper, lead and zinc (average concentrations of 309 mg/kg, 620 mg/kg, 435 mg/kg, and 368 mg/kg, respectively). These concentrations are likely to be due to the former mining

activities in the upland areas, suggesting that the mineralization of these metals is located upstream and their concentrations decrease downstream.

According to Rowlett and Lovell (1994), the concentrations of lead, zinc and chromium in England and Wales were found to be generally higher in the coastal areas and estuaries than areas far away from the coast. This may be an indicator that rivers are very important sources of sediment- related elements in these areas. The author reported that about 80% of Pb, 49% of Zn, and 18% of Cd were from human activity sources such as mining and industrial waste.

Heavy metals and stream sediment association, and the contamination of floodplain soils with heavy metals are significant issues all over the world. For example, Van Driel and Smilde (1990) pointed out that enormous amounts of sediment polluted with heavy metals has been carried out via the Rivers Scheldt, Meuse, and Rhine from Europe to the Netherlands, and hence deposited them in the floodplain soils in periods of flooding. Table 6.6 shows the concentrations of selected heavy metals in floodplain soils and some other sources.

Table 6.6: Concentrations of contaminants in floodplain soils and Clay soil, Sewage sludge, and Compost (mg/kg dry weight) (adopted from Van Driel and Smilde, 1990).

pollutants	Clay soils	Compost	Sewage sludge	Meuse sediment	Rhine sediment
As	13	9	5	49	59
Cd	0.34	6	5	6	9
Cr	73	220	83	322	386
Cu	20	630	455	60	187
Hg	0.2	5	2	0.7	7
Pb	30	900	250	209	265
Zn	76	1650	1190	778	998

It is evident from Table 6.6 that contaminant levels in stream sediments are higher than in clay soils. However, the concentrations of Pb, Cu, and Zn are lower in floodplain sediments than in compost and sewage. Likewise, high concentrations of heavy metals have also been found in the floodplain soils of the Urumea River Valley in Spain, and such levels are considered to be of mining origin (Sanchez *et al*., 1998).

Similarly, Rader *et al.* (1997) recorded a high concentration of heavy metals in the floodplain soils of the River Clark Fork, and such concentrations were attributed to the former mining operations during the 1880s in Montana, USA. In the same way, Marron (1992) found that approximately 29% - 44% of heavy metals from mining waste were accumulated in the floodplain soils of the River Belle Fourche, USA. In Papua New Guinea, Yaru *et al.* (1999) recorded high concentrations (889 mg/kg) of copper in the River Fly floodplain soils; such levels suggest a huge amount of Cu-related sediments have been transferred.

Regarding the effects of flooding, floods play a substantial role in the concentration of metals within floodplain soils. For instance, Albering *et al.* (1999), who investigated the River Meuse floodplain soils, pointed out that high concentrations of heavy metals were recorded in soils with a high flooding frequency. The authors also mentioned that floodplain soils that were covered with water once every 50 years have lower amounts of pollutants than soils that were inundated more frequently. However, floods are considered to be the main driver for carrying and transferring heavy metals that are associated with floodplain soils (Ciszewski, 2001).

It was found that floodplain soils sometimes have relatively high levels of heavy metals even in areas of minimum industrialisation; this is likely to be due to the

relationship between heavy metals and stream sediments. For example, in west central Germany, moderate concentrations of heavy metals were found in the floodplain soils of the River Lahn although this river does not flow through industrial areas (Martin, 1997). In this investigation, the author found that copper, lead and zinc had concentrations of 1.5, 2, and 2 times more than their background amount. Finally, it is worth mentioning that after heavy metals have been deposited and accumulated in floodplain soils, they can stay there for a long period of time under stationary conditions. However, they might be moved and transferred again when the surrounding conditions, such as the oxidation- reduction potential, pH, or erosion of the river bed, change (Macklin, 1996).

6.4. Distribution of heavy metals across the floodplain soils of the River Manifold

Appraising the distribution patterns of trace elements across floodplain soils is important, as most of these soils, such as those in our study area, are used for crop production and grazing purposes. Therefore, such an assessment will help in estimating the possible adverse effects that potentially toxic metals could pose to human health and other living organisms.

In the case of flooding, whenever flood water covers the soil on the river sides, the velocity of the flow will decrease and, hence, the ability of the river to carry the sediments is decreased. As a result, coarse sediments are deposited near the river bank, and fine particles settle further away from the river channel (Walling *et al.,* 1999b; Zhao *et al.*, 1999). Therefore, according to Alexander and Marriott (1999), the soil materials that are deposited in floodplain soils include particles ranging from clay and silt to fine sand, with coarse sediments being deposited adjacent to the river channel. Many studies have been carried out to investigate how heavy metal

concentrations change from the river bank. For instance, Zhao (2001) found elevated concentrations of Pb and Zn within 50m of the river channel in the floodplain soils of the Cerist River, UK. However, these levels tend to decrease sharply after this point reaches the background levels. Similarly, high concentrations of heavy metals were found to be related to sediments close to the river channel of the Belle Foureche River, USA (Marron, 1992). Tylor (1996) and Martin (2000) studied heavy metal distribution in the floodplain soils of the rivers South Tyne and Lahn respectively, and high levels of heavy metals were found to be associated with sediments adjacent to the river bank. In the River Lahn floodplain soils, Martin (2000) found higher concentrations of copper, lead and zinc over the first 100m from the channel compared with their concentrations beyond this point. On the other hand, other researchers have observed that the concentration of heavy metals tends to increase away from the river bank. Zhao (2001), for example, pointed out that the concentrations of copper, lead, zinc and cobalt are increased away from the river channel and associated with the coarse particles in the floodplain soils of the River Severn, UK, further away from the river bank.

However, Martin (1997) recorded an approximately consistent, except at location 50cm which has high levels, concentrations of heavy metals through the floodplain soils of the River Lahn. The appropriate interpretation of such high levels is that this point is more likely to have a higher flooding frequency, and hence take more metals. Furthermore, the extension of the floodplain area is affecting the amount of deposited sediments and hence the levels of associated heavy metals. Walling *et al*. (2003) studied the heavy metal concentration across the floodplain soils of the Rivers Calder, Aire, and Swale in Yorkshire, UK. They found that the concentrations of Cu, Pb, Zn and Cr were low in the case of the Rivers Aire and Calder, because

these two rivers have a big system of barriers in the lower and middle reaches, which eliminate the area of the floodplains, which subsequently receives a small amount of sediments and sediment-associated pollutants. Another significant factor that influences the distribution of heavy metals through floodplain soils is river activity. According to Zhao (2001), the modes of grain size distribution, to some extent, affect the pattern of heavy metal distribution across floodplain soils. In addition, due to the unstable nature of floodplains, heavy metals will redistributed over the floodplain soils in the future (Walling and He, 1998).

Figure 6.1 illustrates the distribution of Cu, Pb, Zn, Mn, Cr, Ni, and V across a section through the floodplain soils with an interval of (5 m) from the channel of the River Manifold (for cross section site, refer to Fig. 3.2 in chap. 3). The concentrations of the studied heavy metals in the section of the floodplain soils along a distance from the channel of the River Manifold are shown in Appendix (C).

From Figure 6.1, it can be seen that different metals show different variation modes from the river channel across the floodplain soils. Copper, lead, zinc, and manganese show approximately the same distribution pattern from the river channel. However, the other group of metals (V, Cr, and Ni) shows a distribution pattern that is different from the first group. Over the floodplain soils, the concentrations of the first group of metals generally increase away from the river channel, while the second group of metals appears to have an almost stable distribution from the river channel. Higher levels of Mn and lead were found 40 m away from the river channel. The concentration of Cu reached a peak at 15m from the river channel; it then declined and remained at the same level until 50m away, at which point the metal concentration increased suddenly, reaching about 400 mg/kg. Similarly, Zn had a distribution mode from the river channel similar to that of Cu. Between 5m – 15m

from the river channel, Cr had a concentration of about 35 mg/kg; this then increased suddenly to reach a peak of about 150 mg/kg at a location 20m from the river channel, but this decreased again to the previous level and remained there to the end of the floodplain.

To summarise, the distributions of the metals across the floodplain soils show a number of peaks and depressions at various locations. The majority of the metals show high concentrations close to the river bank within the zone of 20m from the river channel. Likewise, the distribution of heavy metals across floodplain soils elsewhere show similar findings. For instance, the highest concentrations of Cu, Pb, and Zn were found to be located in areas near to the channel of the Lahn River in Germany (Martin, 1997). Moreover, Zhao (2001) found high concentrations of these metals in the Cerist floodplain soils in mid- Wales within a distance of 50m from the river channel. The reason for the high levels of metals adjacent to the river channel is likely to be that the river banks are more frequently flooded compared to areas further away from the channel. As a result, these areas will receive more sediment loads (Bradley and Cox, 1986; Zhao, 2001). Therefore, high concentrations of sediment related heavy metals are likely to be recorded at locations close to the river bank. It is well known that heavy metals are associated with coarse grain particles, which are usually deposited and accumulate close to the river bank. However, metals linked with fine grain particles were found to have high levels further away from the river channel. This might be why high concentrations of Cu, Pb, Zn, Mn, and V were recorded in the studied section. Similarly, a high concentration of Mn was recorded by Bradley and Cox (1986), and this correlated with the size <63µm (fine sand).

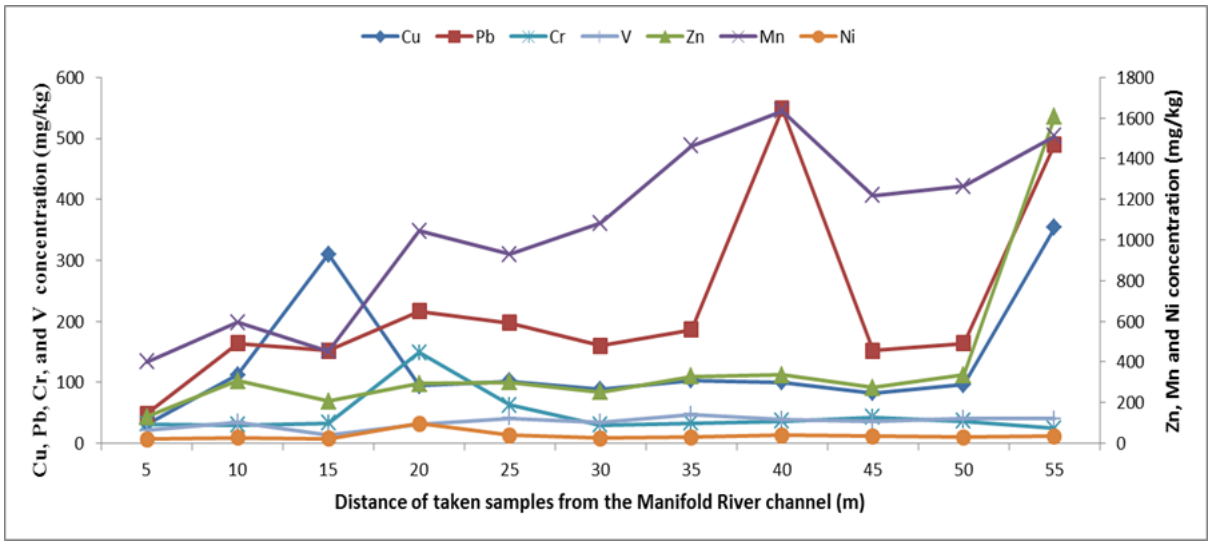


Figure 6.1: Showing the variation in selected heavy metal concentrations across the floodplain soils with an interval distance of (5m) from the Manifold River channel.

6.5. Regression analysis to predict the concentrations of the selected heavy metals with distance from the River Manifold channel across the floodplain soils

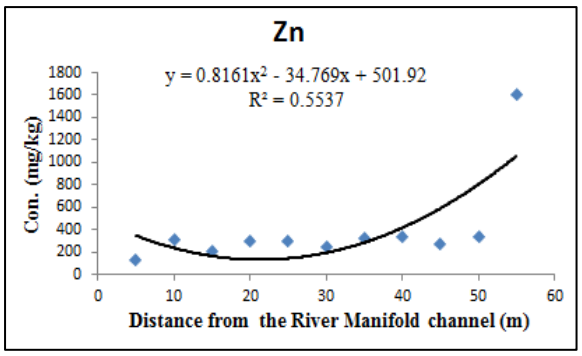
In the previous section, the distribution mode of the studied heavy metals with distance from the river channel was investigated for the floodplain soil samples. This section will describe a mathematical method, i.e. regression analysis, which was used to find out whether there is a relationship between the distributions of the studied pollutants' concentrations and the distance from the river channel across the floodplain soils in the study area. Therefore, bivariate regression analysis was used to find a mathematical equation that connects two variables, the distance from the river channel (X-axis) and the metals' concentrations in the floodplain soils (Y- axis). The main purpose of this method is to find the best line between the two variables (i.e. distance and metal concentration) with the highest possible correlation coefficient (R^2) value. Since the correlation coefficient R^2 has a range between (0) and (1), the strongest relationship between the two variables will occur when the R^2 value is equal to (1) and all of the points lie on the fitted line; as a result the Y values

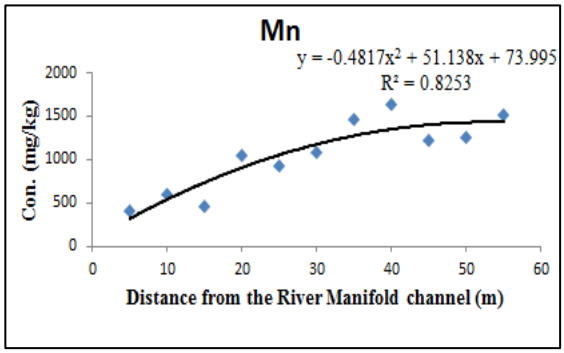
can be appraised from the X values. However, there is no relation between the investigated variables when the R^2 value is equal to (0) (Rogerson, 2001).

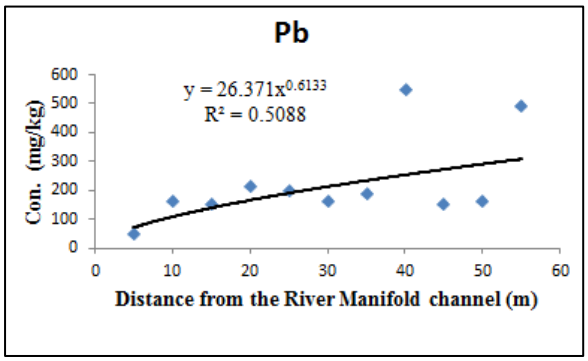
The regression equations that describe the best fit lines between the heavy metals concentrations of the floodplain samples and the distance from the river channel were found using various regression functions, including polynomial, potential, linear, and logarithmic (Fig. 6.2). From Fig. 6.2, it can be seen that among all of studied heavy metals from the floodplain soils Mn has a best fit line regression equation with the highest R^2 (0.8253), whereas Ni has the lower R^2 value (0.0856). For all of the investigated elements in the floodplain soils, the R^2 amounts reduce in the following order: Mn > Zn > Pb > V > Cu > Cr > Ni.

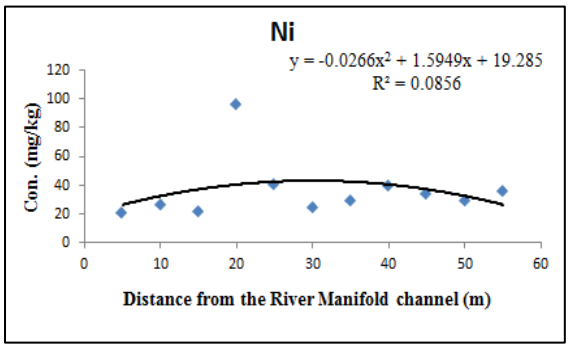
The increasing amounts of Mn, Pb, Zn, and V with distance from the Manifold River channel were interpreted using the quadratic function of regression analysis, except for Pb, which is best explained using the power function of regression analysis.

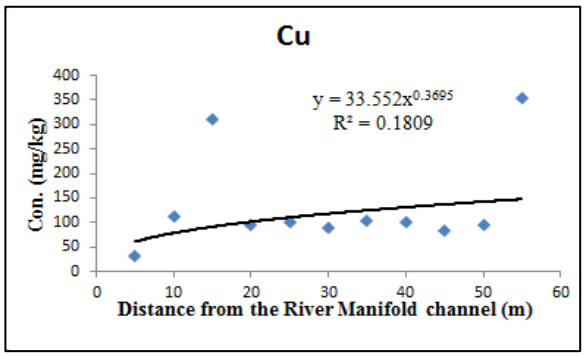
These four metals have fairly high R^2 values, and as a result their concentrations can be calculated from the distance data using regression analysis. However, Cu, Cr, and, Ni concentrations generally decrease with distance and are well explained using quadratic equations, except Cu which has the fit regression line using power function. These three metals show a poor relationship with the distance from the river channel with lower R^2 values of 0.1809 for Cu, 0.547 for Cr and 0.0856 for Ni. As a consequence, the concentrations of these metals cannot be estimated on the basis of distance data by regression analysis.

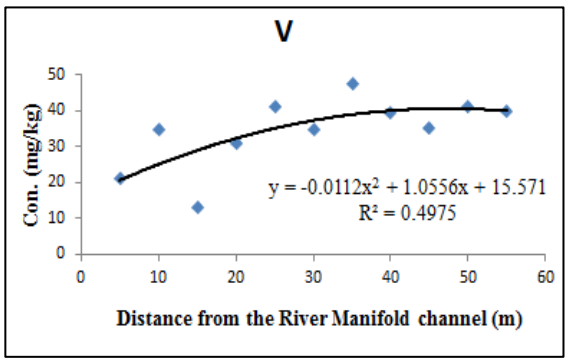












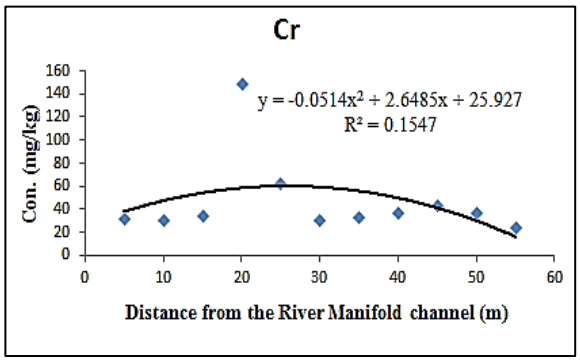


Figure 6.2: Showing the best fit lines, equations, and R- squared amounts for selected heavy metals concentrations of floodplain soils with distance from the channel of the River Manifold at study area

Tt is worth noting that the lower R^2 values for some elements as in the case of Cu, Ni and Cr are more likely attributed to the presence of one or two outliers in some localities, which are either due to the contamination effect while performing soil analysis or they represent localised high values. These high values (outliers) seem to be due to the presence some depressions along the sampling section that make some locations receive more flood sediments in comparison with others resulting in high metal values.

However, R^2 values can be increased if some outliers are omitted. For instance, if the Ni value at point (20m) is omitted, the R^2 value increases from 0.08 to 0.43. Likewise, in the case of Zn the R^2 value will increase from 0.55 to 0.74 if the Zn value is taken away at the point of (55m).

To summarise, in the regression analysis, when there is a high R^2 value between the heavy metal concentrations and the distance from the river channel, this means that the distance from the river channel plays a significant role in governing the concentration of the metals of interest over the floodplain soils. Distance has been indicated as a controlling parameter for the distribution of heavy metals across floodplains by other researchers, for instance Zhao et al. (1999). Moreover, Marron (1992) and Bradley and Cox (1990) pointed out that the grain size factor also plays an important role with distance in terms of the distribution of heavy metals across floodplain soils. This is because when floodplain soils are flooded frequently fine grain sediments are distributed away from the river channel, which in turn affects the distribution mode of the metals over the area.

6.6. Correlation and association between selected heavy metals of the floodplain samples

Examining the relationship between pollutants in environmental studies is of great interest as it gives an insight into how metals are related in the system of interest. It is well known that metals belonging to the same source behave similarly to some extent. For instance, according to Dai *et al.* (2004) when metals are associated positively and strongly, such an association gives an indication that they might come from one source or belong to the same source of contamination. One of way of establishing such an association is the Pearson correlation approach; however, the Spearman rank correlation method was applied as the data are not normally distributed. Using SPSS software, the Spearman correlation coefficients (r) between the studied metals in the floodplain were calculated (Table 6.7).

Table 6.7: Spearman rank correlation coefficient of studied metals in the floodplain soil samples at Ecton mining area.

		Cu	Pb	Zn	Mn	Cr	Ni	V
Floodplain samples (N=11)								
Cu	Correlation Coefficient	1.000						
	Sig. (2-tailed)	.						
Pb	Correlation Coefficient	.636*	1.000					
	Sig. (2-tailed)	.035	.					
Zn	Correlation Coefficient	.855**	.782**	1.000				
	Sig. (2-tailed)	.001	.004	.				
Mn	Correlation Coefficient	.427	.282	.591	1.000			
	Sig. (2-tailed)	.190	.401	.056	.			
Cr	Correlation Coefficient	.437	.442	.542	.287	1.000		
	Sig. (2-tailed)	.179	.174	.085	.392	.		
Ni	Correlation Coefficient	.633	.567	.717*	.367	.817**	1.000	
	Sig. (2-tailed)	.067	.112	.030	.332	.007	.	
V	Correlation Coefficient	.664*	.509	.636*	.718*	.442	.433	1.000
	Sig. (2-tailed)	.026	.110	.035	.013	.174	.244	.
*. Correlation is significant at the 0.05 level (2-tailed).								
**. Correlation is significant at the 0.01 level (2-tailed).								

From Table 6.7, it appears that the following pairs of metals, Mn/V and Cr/Ni, are correlated strongly with a positive correlation at a significance level of $p<0.01$ and $p<0.007$, respectively. Likewise, these pairs, Cu/Zn, Cu/Pb, Pb/Zn, Zn/V, and Cu/V, are found to be strongly correlated at a significance level of ($p<0.05$). In addition, from r values (Table 6.7), it is clearly shown that there is no negative correlation between any pair of the metals studied.

Overall, on the basis of both r value and significance level, results indicate that there are two groups of metals in which metals are correlated significantly. The first group includes Cu, Pb, and Zn, whereas the second group includes Cr, Ni and Mn, with V shows an association with both groups. With respect to the first group, such association is most likely due to the fact that Cu, Pb, and Zn are attributed to former mining operations in the area as these metals are available in sulphide minerals such as galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), which were extracted in the area (refer to mineralisation section in chap. 2). Therefore, the best interpretation of the presence of these metals together in floodplain soils is that they were released into the River Manifold channel and then transported downstream where they accumulated in the floodplain soils (Dai *et al*., 2004). On the other hand, the other group does not any correlation with the Cu, Pb, and Zn, suggesting that these metals originated from another source, which might reflect the parent rock composition in the headwaters region. Furthermore, shale outcrop located at the east of the study area (Fig. 2.4) is another possible for this group metals. Similar findings were reported by Bradley and Cox (1986) for the River Hamps, with a poor correlation between Mn, Pb. However, V association with both groups is most likely to indicate that both sources mentioned above are possible sources for V.

6.7. Correlation of investigated heavy metals with organic matter content and pH values in the floodplain samples

The organic matter content for all of the collected samples was determined using the loss of ignition (LOI) method (refer to chap.3 for procedure used). Full statistical data for the organic matter content in all of the samples studied is listed in appendices (K1 and K2). The organic matter content for the floodplain samples ranged from 6.31 % to 22.23% (Table 6.8). The national mean value of organic matter for England and Wales is 3.6% (McGrath and Loveland, 1992). Comparing this amount with our samples, it can be seen that the average amount of organic matter in the floodplain samples (11.37 %) is quite a lot bigger than the average national level in England and Wales. As a consequence, this may provide a relatively bigger surface area and more binding sites to heavy metals for accumulation (Shuman et al., 2002), and finally low bioavailability to plants (Yaru et al., 1999). However, the average level in the stream sediment samples (4.9%) is close to that of the national average in England and Wales (6.2%), and hence the metals are more likely to be available than in the floodplain samples.

Table 6.8: Descriptive statistic of organic matter contents and pH values for collected floodplain samples at Ecton mining area.

Samples	Organic matter contents %	pH
Floodplain samples (N=11)		
Max	22.23	6.99
Min	6.31	5.57
Mean	11.37	5.99
SD	4.30	0.41

Regarding the pH values, all of samples were tested for their pH using the ratio of (1:2.5) soil to deionized water (w/v). The sample pH results are shown in appendices (K1 and K2). From Table 6.8, it can be observed that the pH values of the floodplain ranged from 5.57 to 6.99. The mean pH value was 5.99 for the floodplain samples. The national average pH of the soil in England and Wales is 6.0 (McGrath and Loveland, 1992). Based on this value, the average pH for the floodplain samples was slightly below the national average. Although the study area is underlain by Carboniferous Limestone (refer to chap 2 for geology), the soil samples for all the collected floodplain soils were acidic (pH less than 7). The reason for such acidic conditions, according to McGrath and Loveland (1992), is that the bed rocks (Carboniferous Limestone) are covered by a layer of peat material, which developed in reduced conditions with high amounts of rainfall, which make the soil have an acidic nature.

6.7.1. Correlation between heavy metals and soil pH values in the floodplain samples

There is a strong and positive correlation between Cu and soil pH with a significance level of p <0.05 in the floodplain soils (table 6.9). Similarly, Zn is associated strongly and positively with the soil pH at a significance level of p <0.01.

Table 6.9: Pearson correlation coefficient between studied heavy metals, organic matter, and pH in the floodplain samples at the study area.

	Cu	Pb	Zn	Mn	Cr	Ni	V
Floodplain samples (N=11)							
pH	0.686*	0.288	0.785**	0.138	-0.439	-0.310	.0002
OM%	0.465	0.725*	0.901**	0.733*	-0.120	0.126	0.617*

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Cr and Ni were found to be correlated negatively with pH in the floodplain soils. The positive correlation between Cu, Pb, and Zn in the floodplain soils and Cr and Ni in the stream sediment samples with pH is most likely due to the acidity of the soil in both cases (Table 6.8), as this make these metals present in high concentrations. However, the role of organic matter cannot be ruled out as it acts as a sorbent for metals due to its binding sites.

6.7.2. Correlation between heavy metals and organic matter content in the floodplain samples

On the basis of the (r) amounts in Table 6.9, it is obvious that Pb, Mn, Zn and V in the floodplain samples are positively and strongly correlated with organic content at a significance level of 0.05. (For Zn the significance level was 0.01.) However, Cu concentration has a poor correlation with organic matter value, and there is a negative correlation of Cr with this component. The strong correlation of Pb, Zn, V, and Mn of the floodplain soils with organic matter content is very likely to be due to the presence of these metals in the organically bound phase.

A positive correlation between Cu, Pb and Zn and organic matter was reported by Dai *et al.* (2004), who studied soils contaminated with industrial waste. In addition, a poor correlation between Mn, Cr and Ni and organic matter was found by Bradley and Cox (1986), who collected samples from the Manifold River valley.

Since the floodplain in the current study is mainly used by grazing animals and livestock (Fig. 6.3), the positive correlation of heavy metals with organic matter in this area should be taken into account, as such a correlation may enhance heavy metals in regard to their availability in high concentrations, and consequently they may pose a risk to grazing animals.

Figure 6.3: View of study area showing grazing cattle.

According to Dai *et al.* (2004) high levels of heavy metals prevent the degradation of organic remains. As a result organic matter content is present in large amounts, and hence high levels of heavy metals are expected to be available in the area of interest.

6.8. Correlation between heavy metals and different particle sizes in the floodplain soils

The ratio of the three main fractions of particle size (i.e. sand, silt, and clay) for the collected soil samples was determined using a Malvern Mastersizer facility after the organic matter had been removed using hydrogen peroxide (refer to chap. 3 for particle size distribution section). The sample results are shown in appendix (O).

The reason for estimating these classes, as stated by many researchers, such as Droppo and Jaskot (1995), is that different fractions, especially clay size, play an important role in adsorbing pollutants to the surface of particles due to the big surface area available in this component. To this end, the statistical software SPSS was used to measure the Pearson correlation coefficients (r) between the studied heavy metals and different granulometric classes in the floodplain and stream sediments (Table 6.10).

Table 6.10: Pearson correlation between studied metals and the main three granulometric classes of the floodplain samples at Ecton mining area.

	Cu	Pb	Zn	Mn	Cr	Ni	V
Floodplain samples (N=11)							
clay	.002	.157	.332	.565	.128	.225	.555
Silt	.005	.128	.399	.564	-.053	.043	.629*
sand	.298	-.174	-.336	-.609*	-.149	-.260	-.819**

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

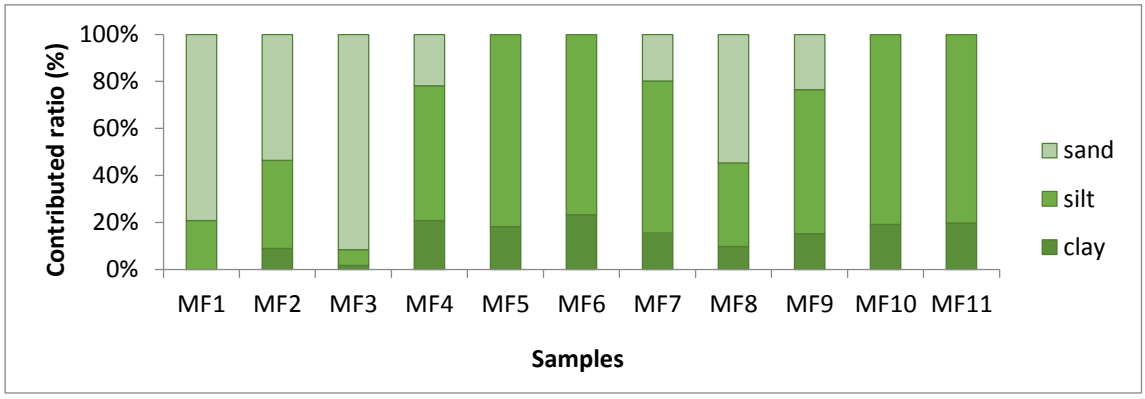


Figure 6.4: Percentage contribution for the main three particle size classes (clay, silt, and sand) in the floodplain samples.

Contribution of clay, silt, and sand for collected floodplain soils are shown in Fig. 6.4. Figure 6.4 shows that clay, sand and silt contribute with different ratios to the samples, with the highest percentages for the sand fraction being found in samples MF1, MF2, MF3, and MF8. However, in the case of samples MF5, MF6, MF10, and MF11, the silt and clay fractions contribute the whole samples without any contribution for sand. Among the samples, except for samples MF1 and MF3, it is obvious that the silt fraction is the dominant granulometric class with almost 80% in samples MF5, MF10, and MF11. It can be seen, however, that the clay fraction contributes a minimal percentage to samples without any presence in sample MF1 (Fig. 6.4).

Pearson correlations, two-tailed, between the investigated heavy metals and the main three granulometric classes are shown in Table 6.10. It can be seen, generally, that all of the studied heavy metals are correlated positively with both the clay and sand fractions, except for Cr, which has a negative relationship, with the highest association for manganese, vanadium, and zinc. Such positive correlations have been found elsewhere by other researchers, such as Esmaeili et al. (2014), Paramasivan et al. (2015) and Suresh et al. (2015), except with Cr, which has a negative correlation. The best explanation for the positive correlation that these metals have with clay is that this fraction is well known to be a good sorbent for pollutants due to its high surface area. According to Suresh et al. (2011), fine size fractions, especially the clay class, have the ability to absorb cations as they are negatively charged and have a high cation exchange capacity (CEC).

However, all of the metals studied, except Cu, have a negative correlation with the sand fraction, with the most significant negative association being for V at a significance level of < 0.01. Negative associations of the heavy metals with sand

have been found in other studies, for instance Lv et al. (2014). In addition, from Table 6.10 it is obvious that the correlation of the metals with the silt fraction, particularly vanadium, is stronger than with clay size. As mentioned by Morton-Bermea et al. (2009), this is likely to be due to the presence of magnetic minerals in the silt grains, which act as a sorbent for heavy metals to the surface of this fraction, and thus make their concentration to be elevated.

6.9. Summary

The distribution of the examined metals (Cu, Pb, Zn, Mn, Cr, Ni, and V) across a section through a selected floodplain, with an interval of 5m from the channel of the Manifold River, was investigated. The results indicate that there are two patterns of distribution from the River Manifold channel. The first pattern includes Cu, Pb, Zn, and Mn. These metals show a similar trend of distribution through the floodplain with the general levels increasing away from the river channel. However, the second pattern of distribution includes Cr, Ni, and V, which demonstrate approximately a stable form of distribution from the river channel. Generally, the majority of the metals show high concentrations close to the river bank within the zone of 20m from the river channel.

Regression analysis technique was applied to find out the possibility of using the distance as a factor to predict the concentrations of metals being studied. Different regression equations were used, including polynomial, potential, linear and logarithmic, and the results show that Mn has a best fit regression equation with the highest R^2 amount of 0.8253, whereas Ni demonstrates the lowest R^2 value of 0.0856. For all of the investigated elements in the floodplain soils, the R^2 amount showed a general reduction trend as follows: Mn > Zn > Pb > V > Cu > Cr > Ni. It should be held in mind that, although R^2 amount is slow for some metals such as Cr

and Ni due to the presence of some outliers, which might introduced because of contamination whilst sample analysis, the R^2 values can be increased by omitting these abnormal values. As a result, R^2 would increase as in the case of Ni for which R^2 values will be improved from 0.08 to 0.43 if Ni value at 20m distance is omitted.

The correlation and association between the studied heavy metals in the floodplain was examined using correlation matrix. Such a relationship gives an insight into how metals relate together in the system of interest because metals belonging to the same source behave similarly to some extent. The results demonstrate that Cu, Pb, Zn are associated with a fairly strong correlation, whilst a weak correlation was shown between Cr, Ni, and V, indicating that Cu, Pb, Zn are most likely to be derived from the same source, which might be attributed to the former mining operations in the study area.

The correlation of the metals studied with organic matter content and soil pH for the floodplain samples was also determined. The results indicate that Cu, Pb, Zn, and Mn are correlated positively with the pH value, with Zn showing a strong positive correlation at a significance level of 0.01. Regarding the organic matter content, Cu, Pb, Zn, and Mn showed a positive association with organic matter content.

For the floodplain samples, the metals studied have been correlated with the main three granulometric classes (i.e. clay, silt, and sand). The results demonstrate that all of the studied heavy metals are correlated positively with both the clay and silt fractions, except for Cr, which has a negative association, with the highest association being for manganese, vanadium, and Zinc. This may indicate the role of clay in adsorbing these metals.

Chapter Seven: Characterization of speciation, leachability, and acidification of selected heavy metals from topsoil samples at Ecton mining area

In this chapter each part will be treated separately. Firstly, the specific soil parameters that effect distribution of heavy metals such as total organic carbon, pH, Eh, different granulometric classes (clay, silt, and sand), and cation exchange capacity will be illustrated. Then, the influence of these factors on the speciation and leachability of the studied metals (i.e. copper, lead, zinc, manganese, chromium, nickel, and vanadium) will be discussed using statistical methods such as Principal Component Analysis (PCA), and the Pearson correlation coefficient. Finally, the consequences of acidification and how changes in the site pH may affect the mobility and release of the metals being studied at the study area will be analysed.

7.1. Soil specific Factors

7.1.1. Organic matter content

The organic matter amount for all of the collected soil samples was measured using the loss of ignition (LOI) method (refer to chap. 3 for procedure). The total organic carbon (TOC) content was measured using the potassium dichromate approach (refer to chap. 3 for method) described in Radojevic and Bashkin (2006). Since, the total organic carbon measured using this method for the first ten samples was close to that obtained using the following equation:

Organic matter (%) = 1.72 * Organic carbon (%) (Radojevic and Bashkin, 2006)

Therefore, this equation was adopted to measure the content of the TOC for the rest of the samples. All of the results are summarized in appendix (K1). From Figure 7.1, it can be seen that the highest organic matter content is illustrated by sample ES13, 55.53% is organic matter. However, the lowest organic carbon content is

demonstrated by sample ES32, of which just 6.07% is organic carbon (Fig. 7.2). All of the samples except samples ES6, ES13, ES35, and ES37 contain less than 15% TOC. This may indicate that these samples are exceptions because during the loss of ignition process some sources of error cannot be discounted, such as the thermal degradation of some other soil components (Vieira-Coelho *et al*., 2002).

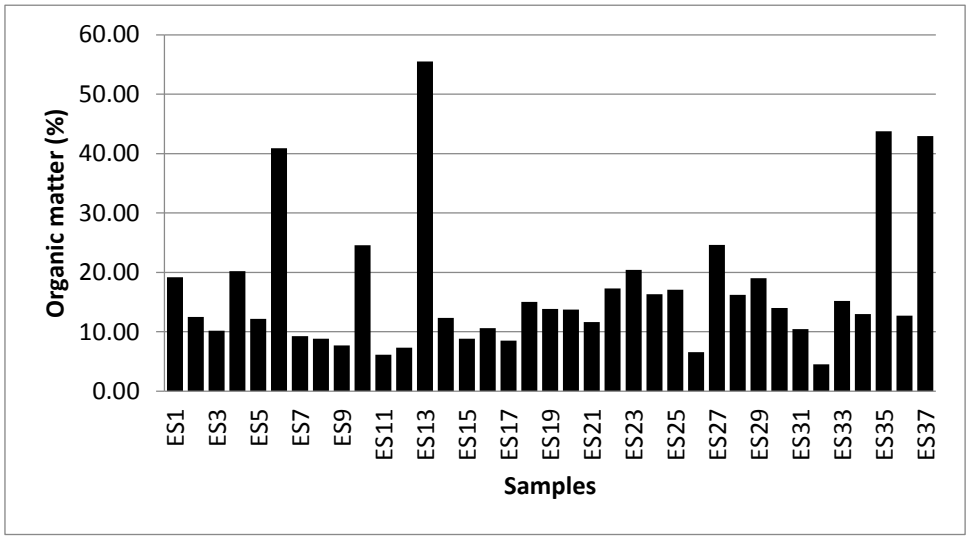


Figure 7.1: Showing the organic matter content of the topsoil samples at the study area.

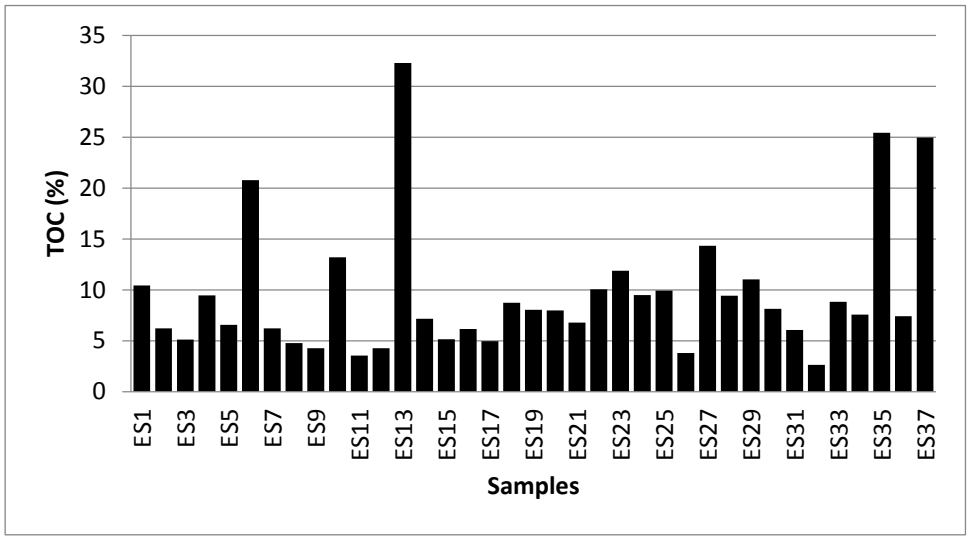


Figure 7.2: Total organic carbon in the topsoil soil samples at the study area.

7.1.2. Grain size distribution

The main particle size classes (i.e. clay, silt, and sand) for all of the samples were examined and the results are shown in Figure 7.3. Figure 7.3 shows that there is a big variation in the percentage of the three main granulometric classes in the collected topsoil samples. Clay's contribution varies from 1.1% in sample ES37 to 46.5% in sample ES11. It is obvious that silt and sand make up most of the total mass, with no sand being found in the case of samples ES1, ES3, ES8, ES11, ES13, ES16, and ES8. Although the sand fraction does appear any contribution in the samples mentioned above, this class present the most of the soil in the case of the samples ES7, ES20, ES30, ES31, and ES37. Clay and sand were not present in some samples, for instance ES1, ES2, ES20, and ES29, whereas the silt size was fraction which has a contribution in the all samples. On the basis of the mean percentage of the different granulometric classes, Figure 7.4 shows that the silt fraction is the dominant class in the study area, with a mean percentage of 52%, whereas the clay fraction has a mean percentage of just 7%.

7.1.3. Soil pH

In the current study, the mean pH value for the topsoil samples collected from the study area was 6.5, a little under the neutral value, which indicates a slightly acidic environment. The highest pH was recorded in sample ES5 (pH 7.8), whereas the lowest pH was found in sample ES16 (pH 5.2) Figure 7.5. Generally, it can be seen that all of the examined samples had a pH of more than 5 and less than 7.5, except sample ES5, for which a value of 7.75 was recorded.

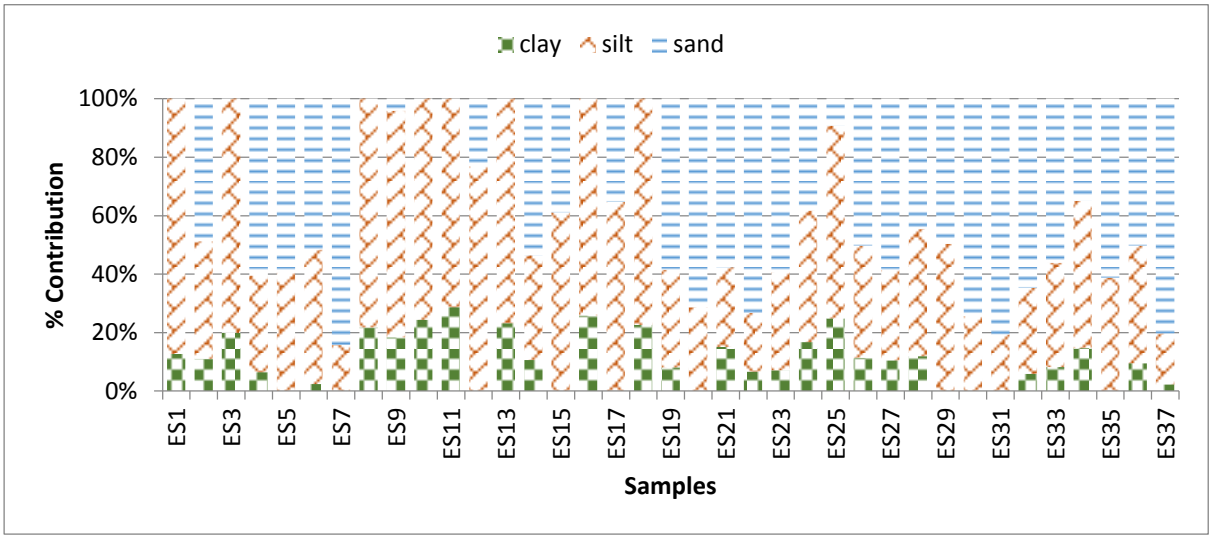


Figure 7.3: The contribution of the main three granulometric classes, clay, silt and sand, to the topsoil samples at the study area.

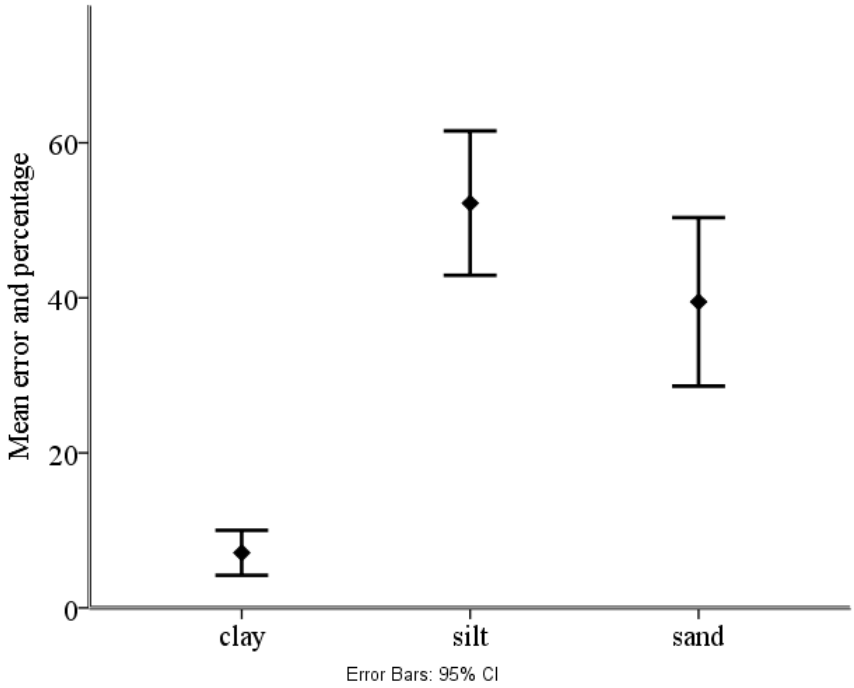


Figure 7.4: The mean error and percentage of the particle size distributing of topsoil samples at the study area.

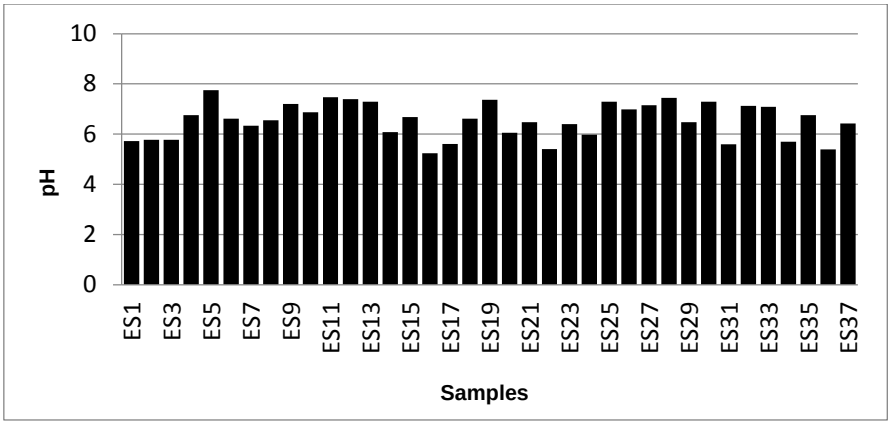


Figure 7.5: pH values for the collected topsoil samples from the study area

7.1.4. Soil oxidation-reduction potential (Eh)

From Figure 7.6, it is obvious that there is a marked variation in the Eh value between the studied soil samples across the study area. The redox potential readings ranged from a maximum value of 218mV in sample ES26 to a minimum value of -264mV in sample ES34. The majority of the samples had Eh values of between 100mV and -160mV, except samples ES5, ES26, and ES34, suggesting that both conditions, oxic and anoxic, are illustrated in the study area.

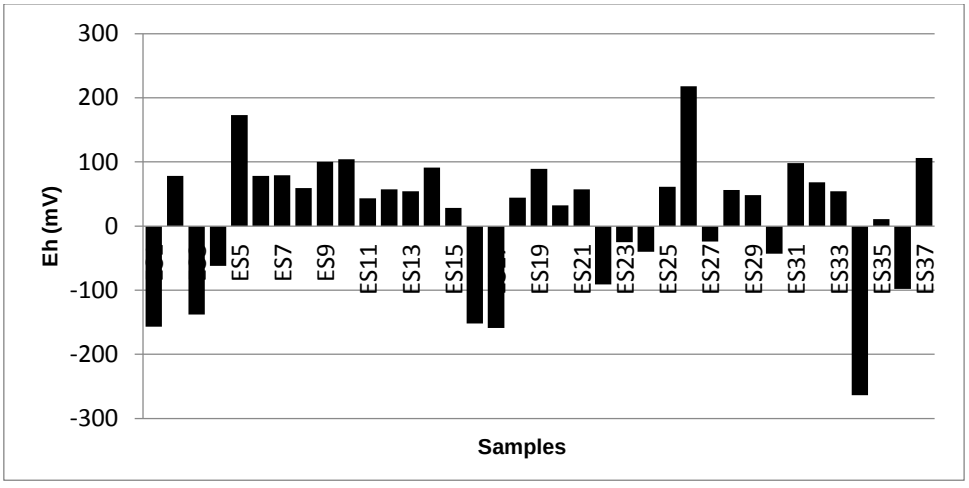


Figure 7.6:Topsoil samples' oxidation-reduction potential (Eh)

7.1.5. Cation exchange capacity (CEC)

The cation exchange capacity for all of soil samples studied was measured using the potassium dichromate procedure, according to Radojevic and Bashkin (2006) (refer to chap. 3 for the procedure used).

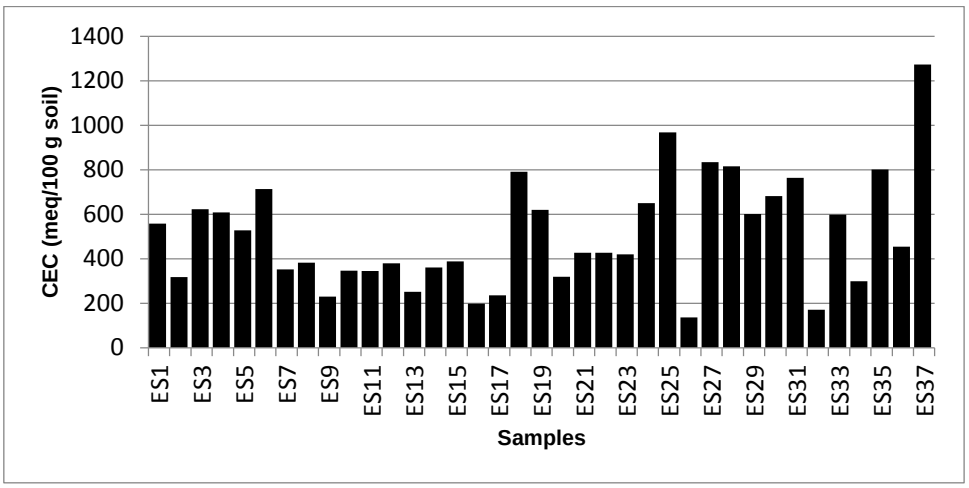


Figure 7.7: Topsoil samples' Cation Exchange Capacity (CEC) quantity

As can be seen from Figure 7.7, sample ES37 demonstrates the highest amount of cation exchange capacity, at 1300 meq/100g soil, followed by sample ES25, in which it is 950meq/100 g soil. All of the other samples contain less than 800meq/100 g soil, with the minimum amount being 100meq/100g soil in sample ES26. It is worth noting that the majority of the samples contained less than 800meq/100 g soil, which indicates that samples containing more than this amount (e.g. samples ES25 and samples ES37) are the exception.

7.2. Total metal concentrations

Figure 7.8 shows the total concentrations of the studied heavy metals (i.e. Cu, Pb, Zn, Mn, Cr, Ni, and V) and some selected major elements, namely Fe and Al, which have a potential role in the distribution of heavy metals. It can be seen that Cu is measurable in all of the samples; the majority of the samples have a Cu value of less

than 500 mg/kg, except for samples ES6, ES7, ES9, ES12, and ES37, in which values of 4502 mg/kg, 1125 mg/kg, 2138 mg/kg, 4775 mg/kg, and 5126 mg/kg, respectively, were recorded (Figure 7.8). The lowest value of Pb was found in sample ES32, which had a level of 29 mg/kg, whereas the peak value was recorded in sample ES7, which had a level of 36644 mg/kg. The zinc concentration varied between 68 mg/kg in sample ES17 and 14378 mg/kg in sample ES37. All of the samples contained more than 500 mg/kg Mn with the exception of samples ES7, ES8, ES12, ES21, ES22, ES30, ES31, and ES32 (Fig. 7.8). There was a large variation in the Mn concentration among the examined samples, with a maximum concentration of 3479 mg/kg in sample ES35 and a minimum concentration of 128mg/kg in sample ES32. Generally, there was a similar trend for Cr, Ni, and V across the studied samples. The highest concentrations of Cr, Ni, and V were present in samples ES24, ES24, and ES22, at levels of 99 mg/kg, 135 mg/kg, and 114 mg/kg, respectively. However, the lowest values were recorded in samples ES32, ES10, and ES32, at levels of 128 mg/kg, 11 mg/kg, and 11 mg/kg, respectively.

7.3. Major element concentrations

The total concentrations of some selected major elements from the collected soil samples are shown in Figure 7.9. Of the five major elements, calcium demonstrates the highest levels, which are above the limits of detection in all of the samples (Figure 7.9). The minimum level of Ca (2640 mg/kg) was found in sample ES16 and the maximum level (276730 mg/kg) was found in sample ES32, followed by sample ES30 (261590 mg/kg). The lowest concentrations were recorded for phosphorus, which was unmeasurable in samples ES11, ES12, ES19, ES26, ES30, and ES32. Except for samples ES10, ES23, ES33 and ES34, all of the other samples showed a

phosphorus concentration of less than 5000 mg/kg. In those samples where P was detectable, the phosphorus level varied from 717 mg/kg in sample ES16 to 17730 mg/kg in sample ES34. Neither Fe nor Al is shown on the graph in sample ES32. There was a maximum of 28851 mg/kg Fe and a minimum of 207 mg/kg Fe in samples ES24 and ES32, respectively, (Figure 7.9). The highest figure for Al was recorded in sample ES27 at a level of 34227 mg/kg, whereas the lowest value was demonstrated in sample ES32, with a value of 182 mg/kg Al. The majority of the samples had a potassium concentration of more than 12000 mg/kg, with a maximum level of 20840 mg/kg and a minimum level of 4650mg/kg in samples ES8 and ES10, respectively. There is an obvious variation in the concentration of these major elements over the study area (Figure 7.9).

7.4. Leaching test

7.4.1. Introduction

In general, leaching can be defined as a process that happens in nature due to the weathering mechanism (chemical and physical) including the reaction between rocks, soils and water, in which metals can be extracted from the solid phase to the liquid phase whenever both phases have connected (Bone *et al.,* 2004). The leaching of contaminant metals from the soil has a significant effect on the local ground and surface water. Therefore, performing a leaching test is of great interest as this will help to examine the probable solubility of the metals under study (Lewin et al. 1994; Sahuquillo *et al.* 2002). According to Heasman *et al.,* (1997), the solubility of the contaminant elements mentioned above is affected by many factors, which can be classified into three main groups: chemical, physical, and biological.

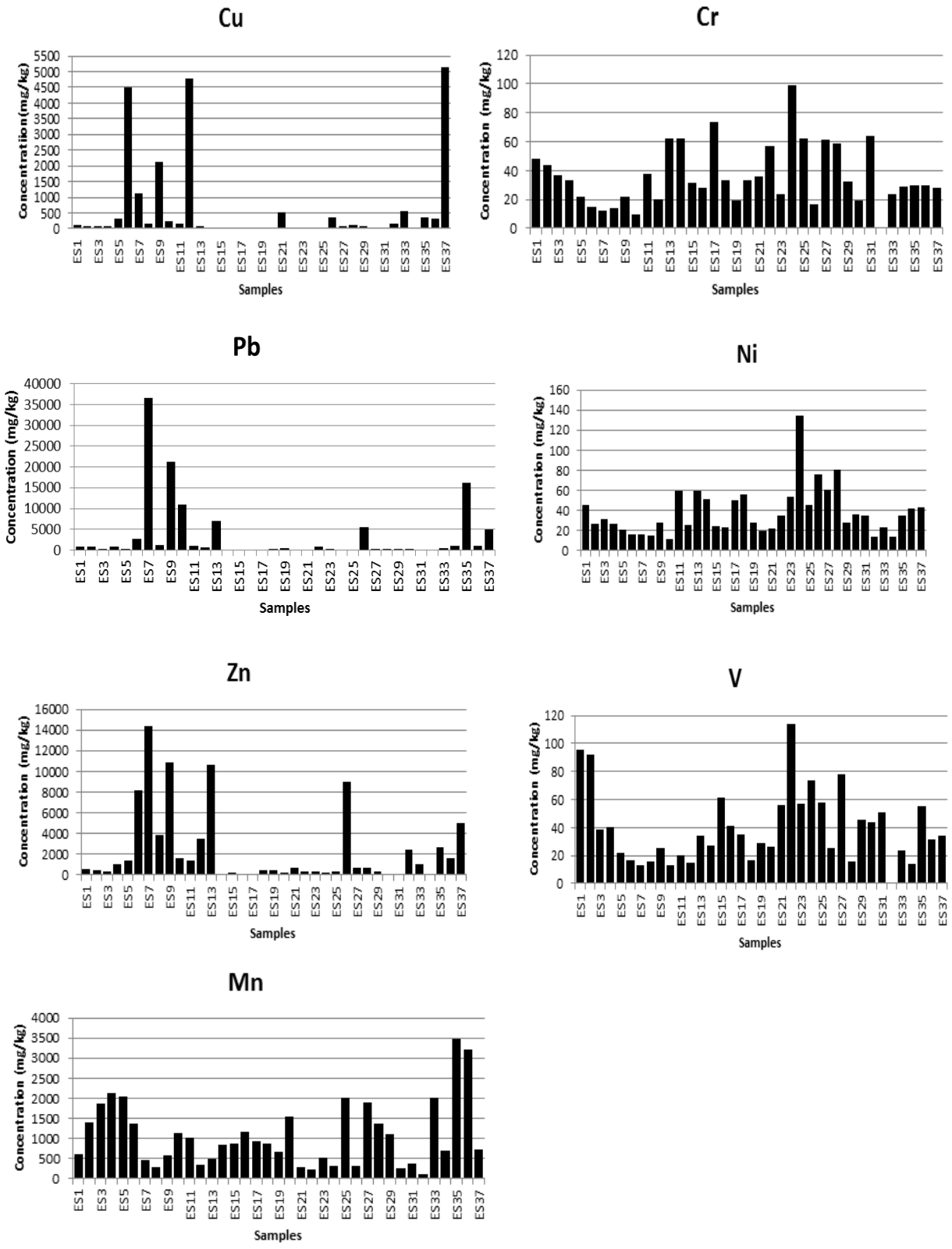


Figure 7.8: Total heavy metals extracted using aqua regia microwave digestion at different time setting.

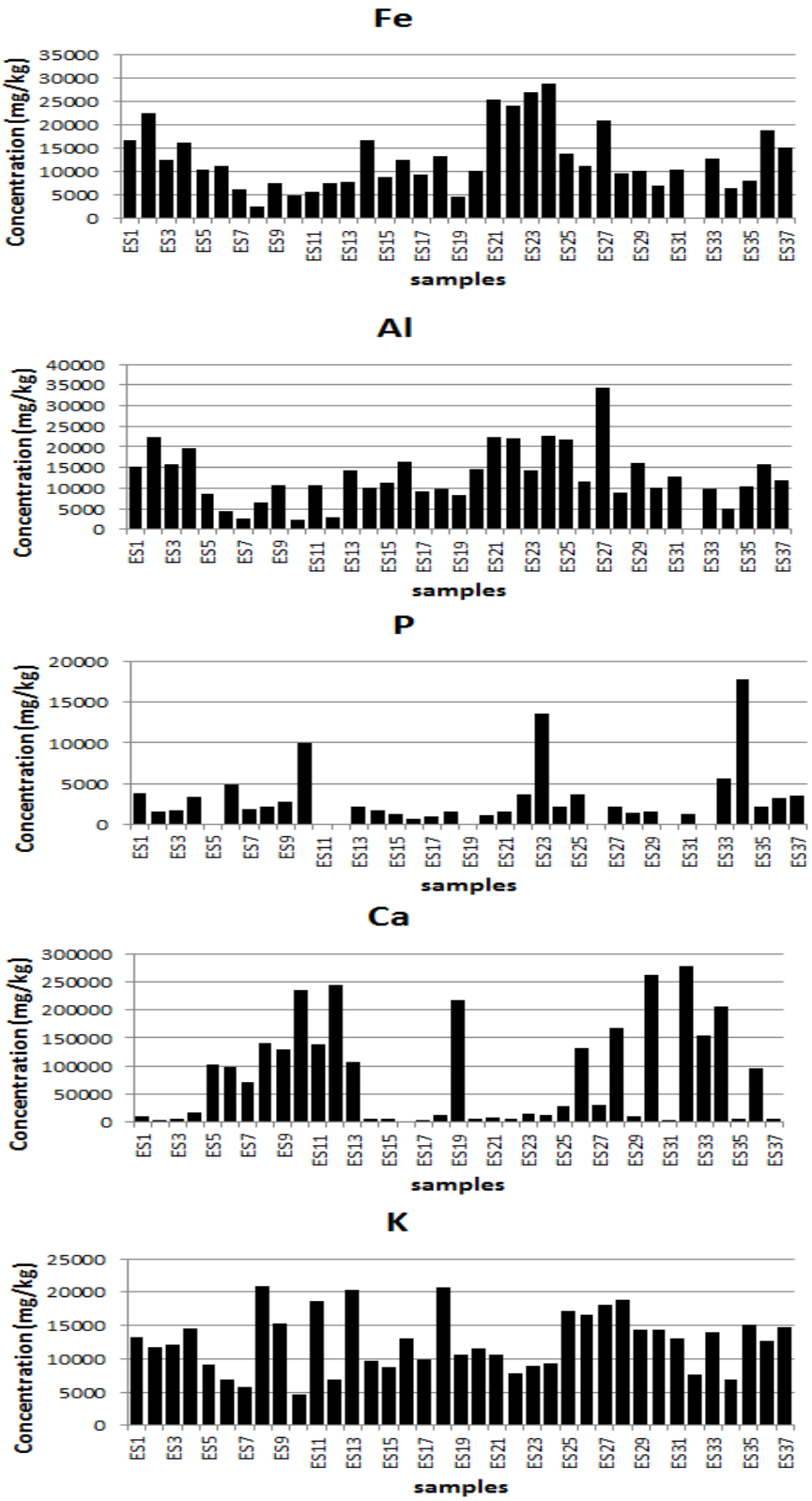


Figure 7.9: Total concentration of some selected major elements

Furthermore, investigating pollutants' solubility using a leaching test is also very important as the solubility of metals is the key indicator of their availability to biota, and hence it is possible to assess the risk that pollutants can pose to the surrounding environment (Rieuwerts *et al.* 1998). As a result, many leaching test methods have been used to examine the potential mobility of the metals under study. Some researchers (e.g. Hartley *et al*., 2004) have used a column leaching procedure in which, in order to estimate the leachability of pollutants, the leachate passes through a column of sample over a limited time, in some cases up to five days (e.g. Jensen *et al.,* 2000). As a consequence, this leaching test method is time consuming and more suitable in the case where only a small number of samples are available. However, in order to assess the leachability of heavy metals in soils, where a large number of samples need to be analysed, other researchers (e.g. Stephens *et al.,* 2001; Lewin *et al.,* 1994) have used the batch leaching test, in which the samples are excited with a specific volume of extractant, in many scenarios deionised water. With respect to the ratio of solid to liquid, many researchers have used different ratios. For example, Stephens *et al.* (2001) used a ratio of 0.5g of sediment to 20 ml of deionised water. Although a solid to liquid ratio of 1:10 is advised by Lewin *et al.* (1994), the authors highlight that using a high liquid to solid ratio may result in reducing the detection limits of the pollutants released. In the batch leaching test, the leachate (i.e. liquid used) has more chance to make contact with the solid particle surface and agitation of mixture also enhanced the process of extracting metals from the sample, so compared with the column leaching procedure, the batch leaching test is likely to be more suitable in extracting pollutants. The problem with using deionised water is that it illustrates the leachability process of the pollutants under conditions of pH and redox potential that are completely different from the actual

conditions, as different soils have different conditions. Therefore, many researchers have tried to manipulate the condition of the soil by adding some acid to the leachate (i.e. deionised water). For instance, Xu *et al*. (1991) used a solution of acidified deionised water and 0.1M NaCl, as this changes the pH of the system and the leachability of the pollutants can be measured under different conditions. However, this may be time consuming in the case of a large number of samples because the pH for each sample needs to be measured to make sure that the required pH has been reached. It should be noted that different types of leachant agents can be used in performing the leaching test; the agent used depends on the objective that the test aims to achieve. For example, according to Heasman *et al.* (1997), in most soil investigations water is the leachant agent, but in other cases such as the evaluation of the mobility of some metal species, a solution of $CaCl_2$ can be used. In addition, in other situations that require more aggressive leachants, a solution of EDTA and acetic acid is more likely to be used. Table 7.1 shows the different types of leachants that can be applied in different situations. Furthermore, in the situation of marine conditions, where the area is exposed to sea water, sea water is the best leachant to simulate the marine conditions (Heasman *et al.,* 1997).

Table 7.1: Different types of leachants with their different aggressiveness level were used for different situation in leaching test. (Adopted from Sloot et al.,1997).

Level of aggressiveness	soil	sediment	waste	Construction materials
Total	Aqua regia	Aqua regia	Aqua regia	Aqua regia
Available for leaching	Acetic acid EDTA	Acetic acid (sequential extraction)	2 step batch test at pH7 and pH4	Not defined
Leaching to reflect environmental conditions	Mild leachants e.g. $CaCl_2$ $NH4NO_3$ $NaNO_3$	$MgCl_2$ $CaCl_2$	Deionised water 5 < pH < 7.5	Deionised water (tank test)

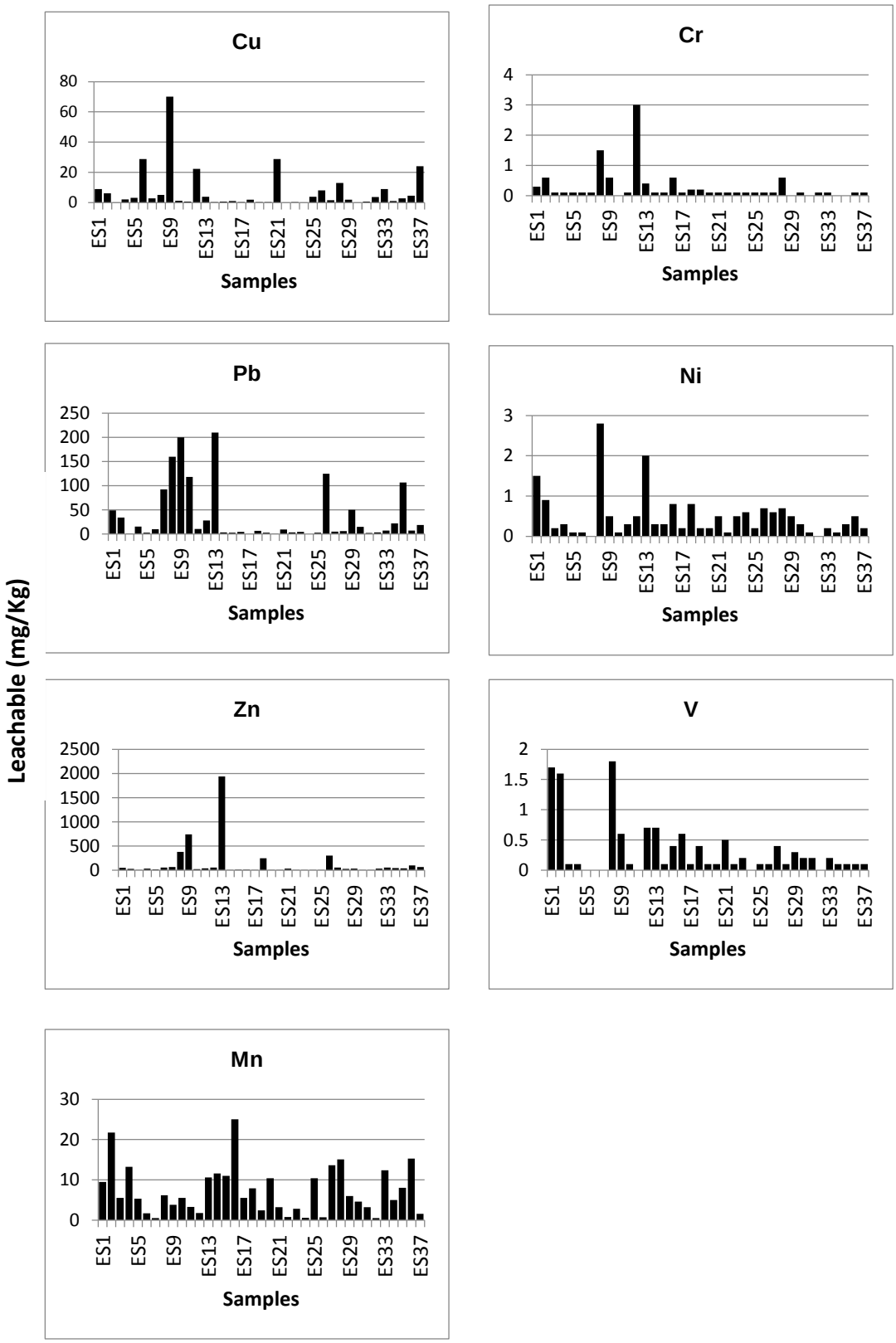


Figure 7.10: Leachable amount (mg/kg) of metals being studied at the study area

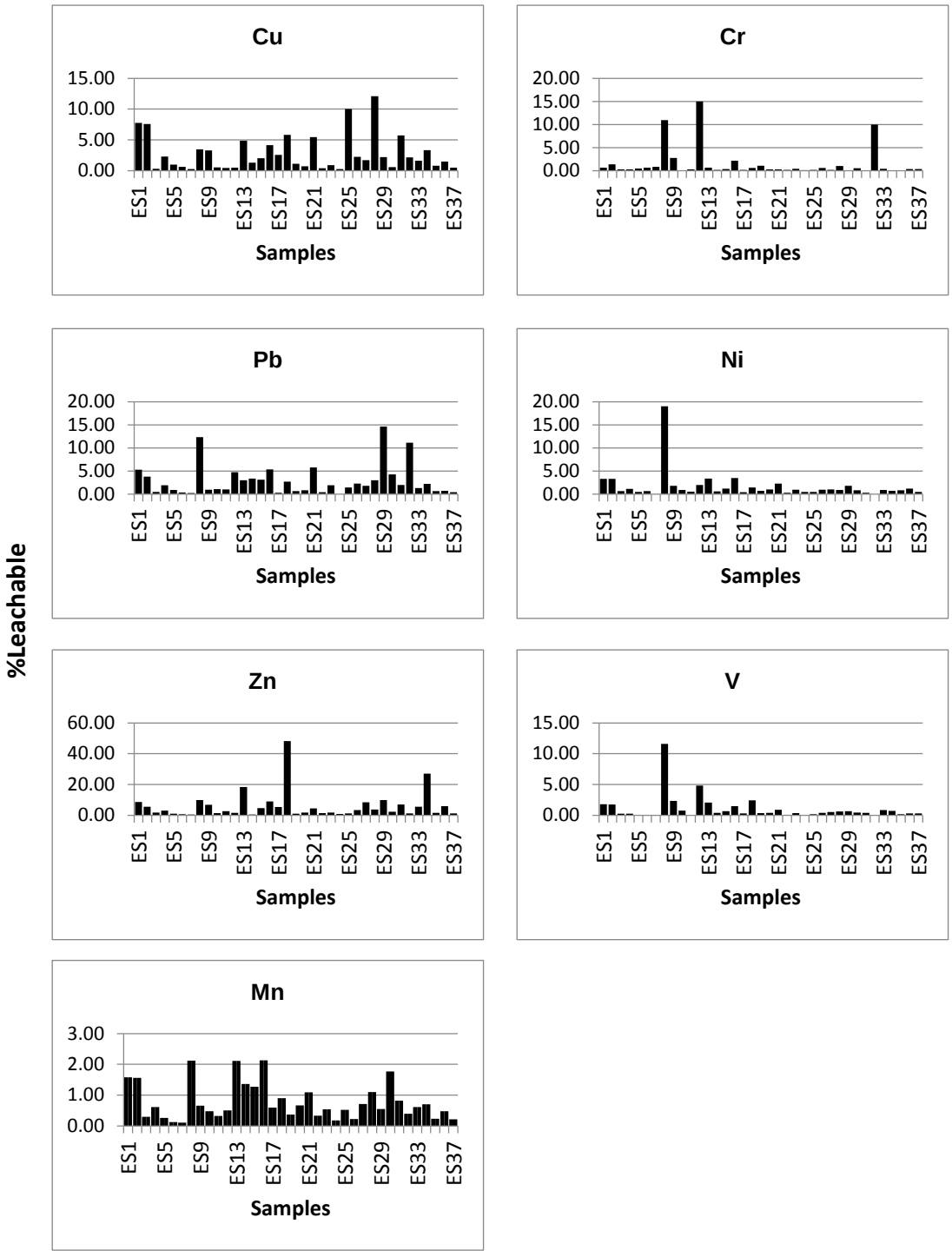


Figure 7.11: % leachable amount of the total metals present

7.4.2. Leachable amount of heavy metals

After the leaching experiment had been performed using deionised water as the leachant, the leachable data were presented in two ways, as the leachable content of the metals in mg/kg and as the percentage of the total metal concentration in the samples. The latter gives valuable information about how leachable the metal is because it represents the total loading of the element in the sample. However, the former method illustrates the amount of a specific substance that can be washed out during a specific time.

From Figure 7.10, it can be seen that Zn has the largest leachable amount among the metals studied, with almost 45% leachable in sample ES18 followed by samples ES34 and ES13, with 25% and 18%, respectively, of the total metal loading (Figure 7.11). Except for samples ES8 for Ni, ES8 for V and ES12 for Cr, Cu and Pb are the next two elements after Zn that have the highest leachable reading, in samples ES28 (12%) and ES29 (14%), of the total metal leachable, respectively (Figure 7.11). Mn shows the least solubility (< 1.5%) in all of the samples except for ES8, ES13, and ES16, for which a leachable amount of just over 2% was recorded. Generally, the majority of the elements have a leachability of less than 5%. Finally, it is worth noting that there is a great variability in the leachability of the different elements over the study area (Figure 7.10).

7.4.3. The association between leachability and soil components

The relationship between the leachable amount of the elements studied and other soil components (i.e. total metal content, pH, Eh, TOC%, and major element content) was examined (Table 7.2).

Table 7.2: Correlation matrix showing the relationship between the percentage leachable and soil specific factors using Pearson correlation coefficient.

		Cu (%)	Pb (%)	Zn (%)	Mn (%)	Cr (%)	Ni (%)	V (%)
Cu (%)	Pearson Correlation	1						
	Sig. (2-tailed)							
	N	37						
Pb (%)	Pearson Correlation	.201	1					
	Sig. (2-tailed)	.234						
	N	37	37					
Zn (%)	Pearson Correlation	.312	.146	1				
	Sig. (2-tailed)	.060	.387					
	N	37	37	37				
Mn (%)	Pearson Correlation	.453**	.441**	.299	1			
	Sig. (2-tailed)	.005	.006	.073				
	N	37	37	37	37			
Cr (%)	Pearson Correlation	-.049	.513**	-.055	.148	1		
	Sig. (2-tailed)	.773	.001	.746	.382			
	N	37	37	37	37	37		
Ni (%)	Pearson Correlation	.163	.545**	.160	.576**	.492**	1	
	Sig. (2-tailed)	.334	.000	.345	.000	.002		
	N	37	37	37	37	37	37	
V (%)	Pearson Correlation	.146	.508**	.248	.510**	.680**	.932**	1
	Sig. (2-tailed)	.390	.001	.139	.001	.000	.000	
	N	37	37	37	37	37	37	37
pH	Pearson Correlation	.035	.017	.021	-.086	.216	.067	.156
	Sig. (2-tailed)	.838	.919	.900	.612	.198	.692	.356
	N	37	37	37	37	37	37	37
Eh(mV)	Pearson Correlation	-.001	.059	-.225	-.178	.145	.021	.072
	Sig. (2-tailed)	.995	.730	.181	.293	.392	.901	.672
	N	37	37	37	37	37	37	37
TOC(%)	Pearson Correlation	-.044	-.189	.069	.021	-.276	-.067	-.124
	Sig. (2-tailed)	.796	.263	.683	.902	.099	.693	.466
	N	37	37	37	37	37	37	37
Fe	Pearson Correlation	.071	-.239	-.069	-.048	-.374*	-.177	-.250
	Sig. (2-tailed)	.678	.154	.683	.777	.022	.295	.135
	N	37	37	37	37	37	37	37
Al	Pearson Correlation	.204	-.105	-.024	.122	-.399*	-.054	-.178
	Sig. (2-tailed)	.226	.537	.887	.472	.015	.752	.292
	N	37	37	37	37	37	37	37
P2O5	Pearson Correlation	-.045	-.164	.215	-.111	-.208	-.052	-.063
	Sig. (2-tailed)	.789	.333	.202	.511	.217	.760	.712
	N	37	37	37	37	37	37	37
K2O	Pearson Correlation	.446**	.174	.387*	.378*	-.057	.378*	.332*
	Sig. (2-tailed)	.006	.302	.018	.021	.736	.021	.044
	N	37	37	37	37	37	37	37
CaO	Pearson Correlation	-.128	.161	-.054	-.035	.483**	.059	.186
	Sig. (2-tailed)	.452	.340	.749	.837	.002	.728	.270
	N	37	37	37	37	37	37	37

The leachable amount of Cu showed a strong positive correlation with leachable Mn and potassium, with a correlation significant level of 0.01. Although the percentage of leachable Pb shows a strong and positive association with the percentage of the total leachable Mn, Cr, Ni, and V, it shows a negative correlation with TOC, Fe, Al, and phosphorous. Leachable Zn shows a significant positive correlation with potassium. The percentage of the total leachable Mn is correlated strongly and positively with Ni, V, and K.

Ni and V exhibit a positive correlation with each other and K as well, but a negative link with phosphorous, aluminium, iron, and TOC.

It was expected that the leachable content of the metals studied would show a negative correlation with those factors that bind these metals to soil, such as TOC and oxides of Fe and Al. The percentage of the total leachable Cu illustrates a negative association with TOC, P, Ca, and Eh (Table 7.2). As a result, increasing the concentration of these factors is linked with a decrease in the concentration of leachable Cu. As the bedrock of the area is mainly Carboniferous Limestone (Refer to chap. 2 for lithology), it is more likely that Ca mainly occurs as a carbonate, which provides further surfaces for metal oxides to be absorbed onto it and increases their absorption capacity (Matera and Le llecho, 2001).

In other words, Ca content retards the leachability of Cu. In the case of TOC, the negative correlation of leachable Cu with this component might indicate that this factor reduces the leachability of Cu due to the adsorption of this element on the functional groups of organic matter surfaces. Soil organic matter is a well-known pool of heavy metals because of their high tendency to make complexes with pollutants (Bai *et al.,* 2012).

Likewise, the negative relationship between phosphorous content and leachable Cu, indicating that P is more likely to minimise the solubility of Cu and it is might be a constituent of the organic matter content of the samples. The best explanation of the positive association between leachable Cu and potassium content is that Cu has been associated with the K-rich clay mineral surfaces such as those of the mica group, which is a significant source of K in the soil (Fanning, *et al.,* 1989).

In addition, the positive correlation exhibited by leachable Cu with leachable Mn is more likely to indicate that there is an association in the leachability behaviour between these two metals. It is also worth noting that leachable Cu is negatively correlated with redox potential, indicating that leachable Cu is more in soil with a minimum oxidizing level. All other metals' leachability behaviour is influenced by factors that have been discussed previously. However, other factors are likely to play a significant role in the leachability of these metals. For instance, lead exhibits a negative correlation with the total content of aluminium and iron. This indicates that the oxides of these metals act as a reducing factor for the leachable amount of lead, which has a tendency to the oxides of these metals (Hudson- Edwards, 2000). As a result, a negative link between lead and the oxides of Fe and Al would have been demonstrated. As in the case of the relationship between leachable Pb and Fe and Al oxides, the percentage of the leachable amount of V, Ni, Cr, and Zn also demonstrates a negative correlation with the total Fe and Al (Table 7.2), indicating that oxides of Fe and Al are restrict these metals and consequently minimise their leachability.

7.5. Principal component analysis

The principal component analysis technique has been used extensively by many researchers to distinguish and determine the possible sources of heavy metals (Xiaojun Wen *et al.,* 2017; Karim *et al*., 2014; Lue *et al*., 2014). Therefore, it is intended in the current study to use this approach to find the relation between the metals being studied, some selected major elements (e.g. iron, aluminium, phosphorus, potassium, and calcium), total organic carbon (TOC %), and cation exchange capacity (CEC mg/100g soil) and different particle size classes (e.g. clay, silt, and sand). The PCA results are shown in Table 7.3. It can be seen that during the analysis of the variance, five components were extracted that explain 71.11% of the total variance. The highest variation in the data is explained by component 1, which demonstrates 26.24% of the entire variance and Fe, Al, V, Ni, and Cr are strongly correlated with (Table 7.4). However, cation exchange capacity and TOC explain a lesser correlation with this component. The main three studied heavy metals (i.e. copper, lead, and zinc), along with calcium show a negative correlation with this component, whilst manganese and phosphorus do not demonstrate any correlation with component 1. With regard to component 2, clay and silt, the fine granulometric classes show a strong positive association with this component and potassium is positively and strongly correlated with this fraction as well but lesser than those of clay and silt.

Cu, Pb, and Zn exhibit a strong and positive link with component 3 with Zn demonstrating a very strong positive relation with this component, which also contains TOC% being correlated with. Component 4 does not show any correlation with the seven heavy metals under study, except for Mn, which demonstrates a fairly strong and positive association with this component, which also shows a strong

correlation with (CEC). Component 5 does not show any correlation with the heavy metals under study, with the exception of Nickel, which has a weak correlation (0.34) with this component.

Table 7.3: Showing principle component analysis results and total variance explained by each component.

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.461	26.240	26.240	4.461	26.240	26.240	3.892	22.892	22.892
2	2.802	16.481	42.721	2.802	16.481	42.721	2.647	15.572	38.464
3	2.047	12.044	54.765	2.047	12.044	54.765	2.221	13.064	51.528
4	1.473	8.662	63.427	1.473	8.662	63.427	1.877	11.044	62.572
5	1.305	7.679	71.106	1.305	7.679	71.106	1.451	8.534	71.106
Extraction Method: Principal Component Analysis.									

From the results of the principal component analysis, some explanation can be drawn with regard to the associations between heavy metals and other soil components, such as oxides of Al and Fe, TOC%, CEC, and soil particle size. The strong association between Cr, Ni, and V with component 1, which also contains Fe and Al being strongly linked with this component, is likely to indicate that oxides of aluminium and iron play a significant role in binding metals by providing binding sites and consequently increasing the adsorption of heavy metals to the surface of these oxides. This has been pointed out by many researchers, such as Shen (1999) and Redman et al. (2002). In addition, organic matter and cation exchange capacity are also involved as a part of this component (i.e. component 1), but show a weaker association (Table 7.4). This might indicate that these soil components, to some extent, act as binding agent of these metals, due to the high cation exchange

capacity of organic matter, as mentioned by Alloway (1995), and therefore make complexes with pollutants.

Table 7.4: Showing principal component analysis results for the soil samples collected from the study area.

Rotated Component Matrix[a]					
	Component				
	1	2	3	4	5
Fe	**.860**	-.173	-.118		-.207
Al	**.831**		-.239	.180	.101
V	**.822**	-.103	-.177		-.114
Cr	**.782**	.136	-.149		.216
Ca	-.740			-.160	
Ni	**.614**	.243			**.377**
clay		**.893**			
sand	.165	-.849	-.108		
silt		**.804**	-.166	-.143	
Zn	-.204		**.919**	-.132	.116
Pb	-.156		**.787**	-.127	
Cu	-.230	-.224	**.559**	.258	
CEC (meq/100g)	.209	-.166		**.795**	.154
Mn			-.213	**.677**	
TOC (%)	**.201**		**.470**	**.654**	-.153
P		.116			-.888
K	.129	**.509**		**.400**	**.579**
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.					
a. Rotation converged in 5 iterations.					

The presence of the fine granulometric classes (i.e. clay and silt) and potassium in component 2 indicate that these fractions are correlated with each other. A possible explanation for this association is that potassium seems to be associated with K-rich clay, such as that related to the mica group, as highlighted by Fanning and Keramidas (1979).

Similarly, the strong association of Cu, Pb, and Zn with TOC% in component 3 indicates that these heavy metals are linked with organic matter. This suggests, as previously mentioned, that organic matter has a tendency to bind contaminants due to its ability for complexation and binding pollutants to the binding sites. Likewise, it can be seen that manganese is well correlated with component 4 (Table 7.4), with also contains organic matter and CEC being strongly associated. This suggests that organic matter is a major soil component that absorbs Mn and controls its concentration on this site because of the high tendency of organic matter in regard to cation exchange capacity and consequently binding heavy metals via complexation.

To sum up, based on the data from the principal component analysis, it can be concluded that oxides of Al and Fe are the key controlling factors of the concentrations of V, Cr, and Ni on this site. These metals are likely to be from a common source, probably as the outcome of parent rocks weathering (genogenic source). However, it seems that Cu, Pb, Zn, and Mn are controlled by the organic matter content and most likely originate from another source, different to that of V, Cr, and Ni. This source seems to be anthropogenic due to the former mining operations in the area. This area, as mentioned previously (refer to mining history section in chap 2), was used for the extraction of copper, lead, and zinc for a long period, resulting in huge quantities of mining waste being disposed of in the surrounding area.

7.6. Fractionation of heavy metals and some selected major elements:

7.6.1. Introduction

The key idea beyond performing speciation of heavy metals in soil and sediments is to assess how changing conditions can affect metal release into the surrounding environment (Tack and Verloo, 1995).

To this end, different approaches have been used by various researchers with different chemical regents being utilised. Sequential extraction is the most commonly used method. According to Tessier *et al.* (1979), metals can be fractionated into five groups: exchangeable fraction, bound to carbonate fraction, bound to Fe/Mn oxides fraction, bound to organic matter fraction, and residual phase. However, the Community Bureau of Reference (BRC) recommends a three-step extraction procedure in which the extracted metals can be divided into three phases: the exchangeable, reducible, and oxidisible phases (Thomas *et al*., 1994). In the current study, fractionation of the metals being studied was assessed using the modified method, described in Ure *et al.* (1993). Based on this approach, the metals are classified into five phases (refer to chap. 3 for procedure details): the exchangeable phase, the bound to carbonate fraction, the bound to Fe/Mn fraction, the bound to organic and sulphide phase, and the residual phase.

7.6.2. Results

Generally, all of the metals being studied were extractable in the majority of the samples and within the detection limits of all of the extractants. Figure 7.12 illustrates the concentration ratio of the trace and major elements extracted in the five metal phases (i.e. exchangeable, carbonate, Fe/Mn oxides, organic and sulphides, and residual fractions). The studied metals were also represented on the basis of the mean concentration of each element presented in each operationally determined phase (Figure 7.13). Copper, lead, and zinc are mostly extracted from the organic phase (Figure 7.13). With the exception of manganese, which is associated mainly with the Fe/Mn fraction, all of other metals (i.e. Cr, Ni, V, Fe, and Al) are mostly associated with the residual phase.

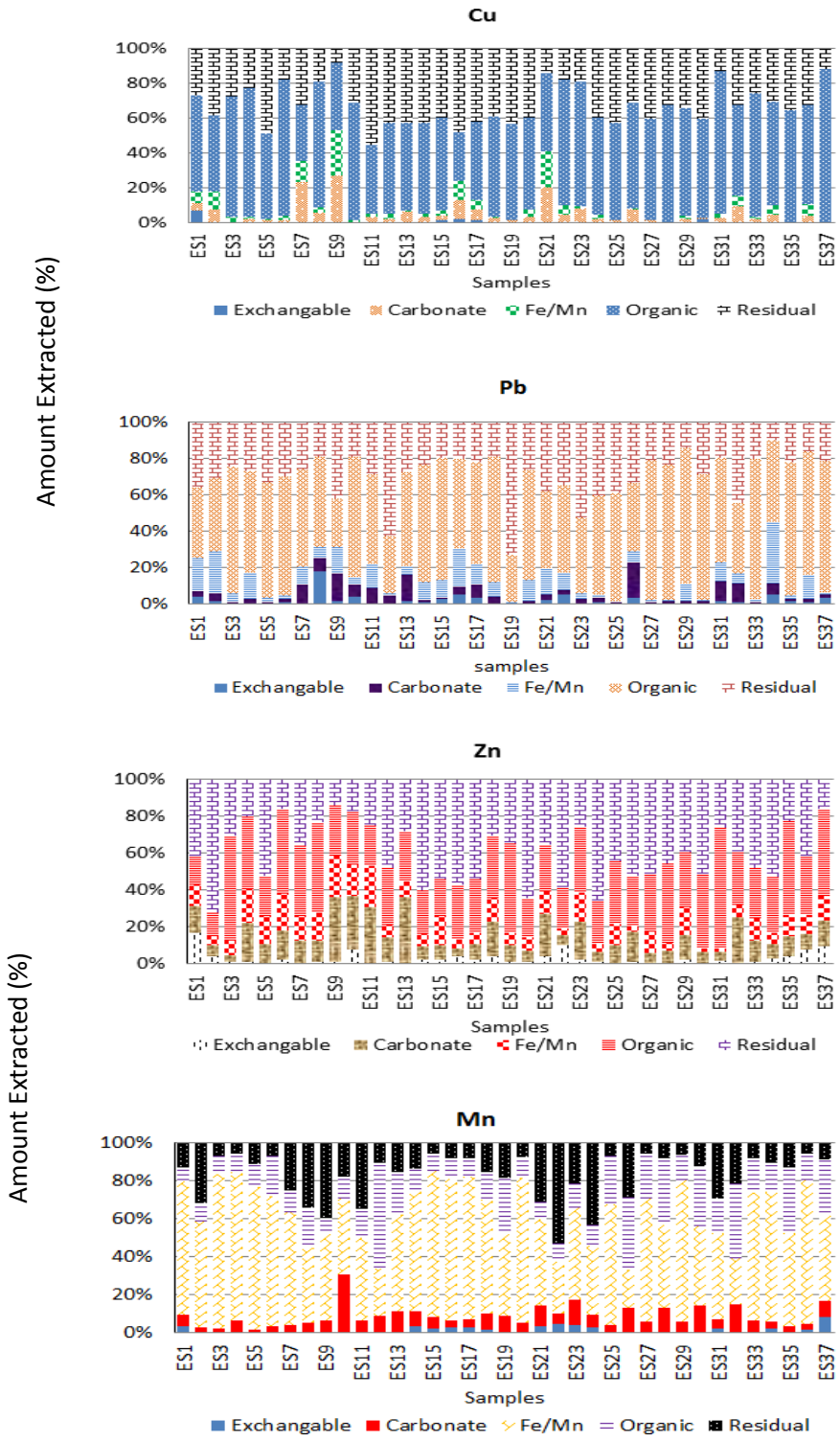


Figure 7.12: Speciation of metals to different soil phases/ continues next page.

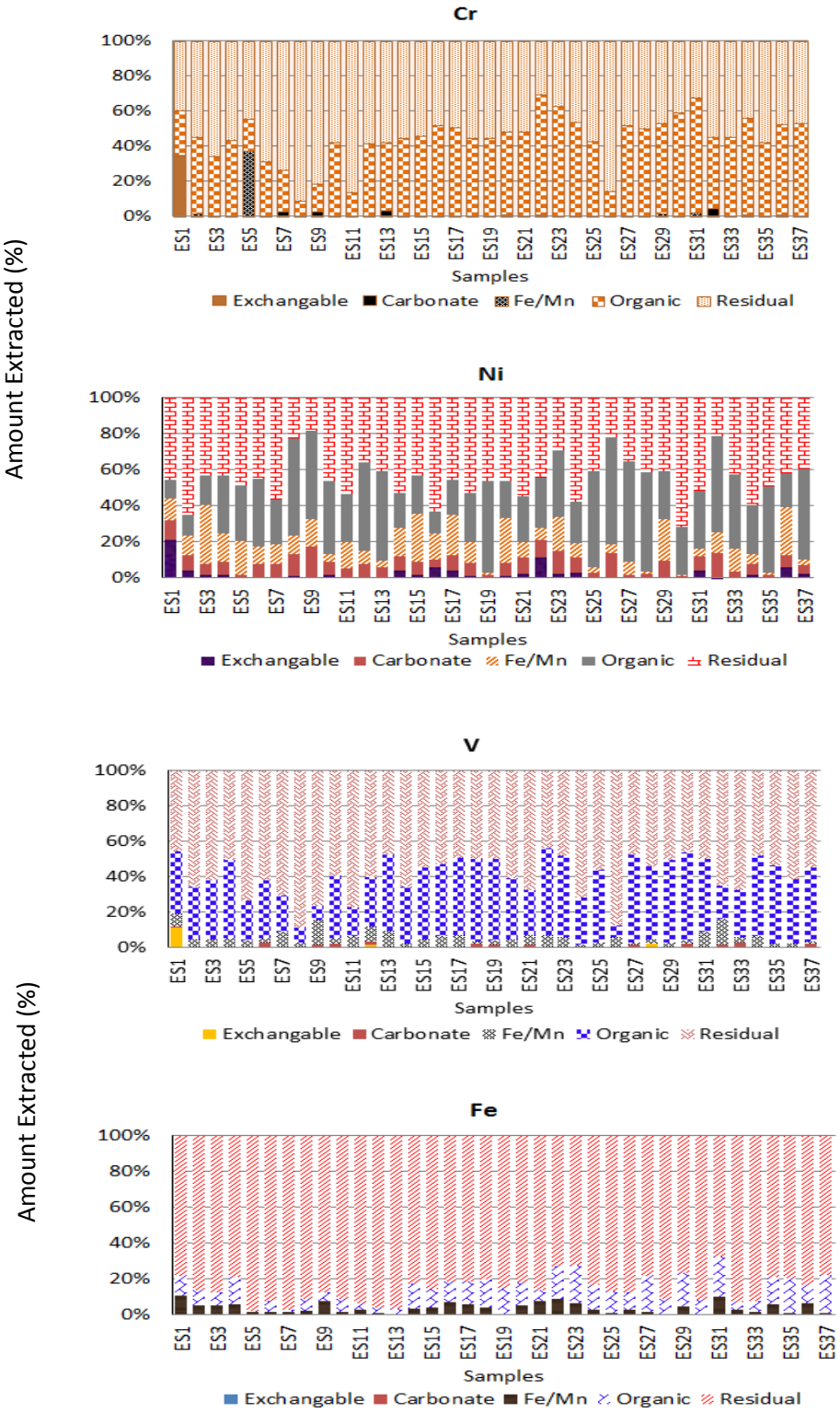


Figure 7.12: Speciation of metals to various soil phases - continues next page.

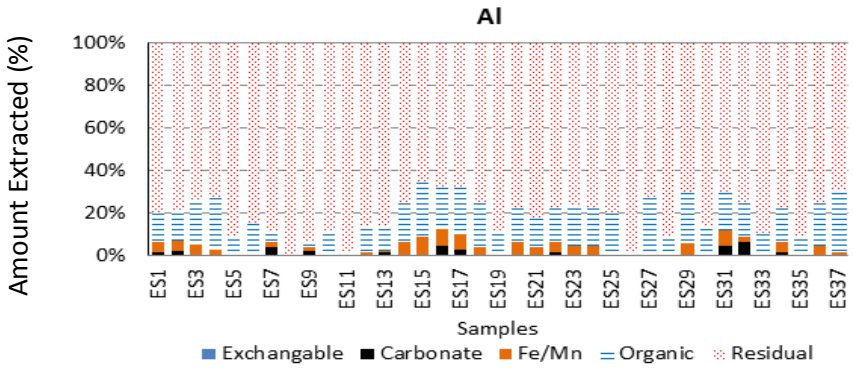


Figure 7.12: (Continued): Speciation of metals to various soil phases

Regarding extractable Cu, with the exception of samples ES2, ES5, ES7, ES9, ES11, ES16 and ES21, copper is more extractable from the organic phase than any of the other fractions. However, the minimum extractable Cu was found in the exchangeable phase with no concentration being recorded in samples ES3, ES5, ES7, ES8, ES9, ES26, and ES32. In the same way, a substantial amount of extractable Cu was found to be associated with the residual phase in all of the samples, but these concentrations were less than those extracted from the organic fraction. Likewise, Pb has the greatest amount extractable from the organic phase. From Figure 7.12, it can be seen that lead was more extractable from this phase than the other phases combined in the case of samples ES3, ES4, ES5, ES6, ES10, ES18, ES20, ES27, ES28, ES29, ES30, ES33, ES35, and ES37. In contrast, the lowest Pb was extracted from the exchangeable phase with no amount being demonstrated in the case of samples ES3, ES7, ES25, ES27, ES28, ES29 and ES30. In addition, a remarkable level of Pb was recorded from the residual phase and approximately the same amount was found in samples ES12, ES13, ES14, ES15, ES17, ES19, ES25, ES27 and ES30. In the case of zinc, the extractable

amount was dominated by the organic matter phase followed by the residual fraction, which was relatively less when compared to that of organic matter (Figure 7.12).

It can be seen from Figure 7.13 that there is more Zn associated with the carbonate and Fe/Mn phases than in the case of Cu and Pb. In addition, a substantial amount of zinc was extracted in samples ES9, ES10, ES11, ES13 and ES 32; this accounted for approximately a third of the total amount extracted. Furthermore, zinc shows relatively more variation between the different phases compared to the case of Cu and Pb. With regard to manganese, it can be seen from Figure 7.13 that Mn is mostly associated with the phase of Fe/Mn, whereas a noticeable amount was also found to be extractable from the both organic and residual phases. In all of the samples, with the exception of samples ES2, ES8, ES9, ES10, ES11, ES12, ES19, ES 22, ES24, E28, ES32, and ES32, the amount of zinc was more in the Fe/Mn phase than in all of the other phases combined (Figure 7.12). With the exception of samples ES11, ES22 and ES36, less zinc is associated with the exchangeable phase.

From Figure 7.13, it can be seen that Cr, Ni, V, Al, and Fe were mainly extracted from the residual fraction phase. Although Cr is dominated by the residual phase, this amount is relatively similar to that extracted from the organic phase. The graph does not show any chromium extracted in either the exchangeable or Fe/Mn phases for any of the samples, with the exception of sample ES1 for exchangeable, ES5 for the carbonate fraction, and ES7, ES9, ES17, and ES33 where Cr was extracted. With the exception of samples ES1, ES15, ES16, ES22, ES31 and ES35, nickel was recorded as having the lowest extractable amount in the exchangeable phase. However, Ni presented a substantial amount in all other phases (i.e. carbonate, Fe/Mn oxides, organic, and residual fractions). In addition, Ni showed a high

variation in the level extracted among the samples. Like Ni, vanadium was found to be extracted in all of the phases of all of the samples.

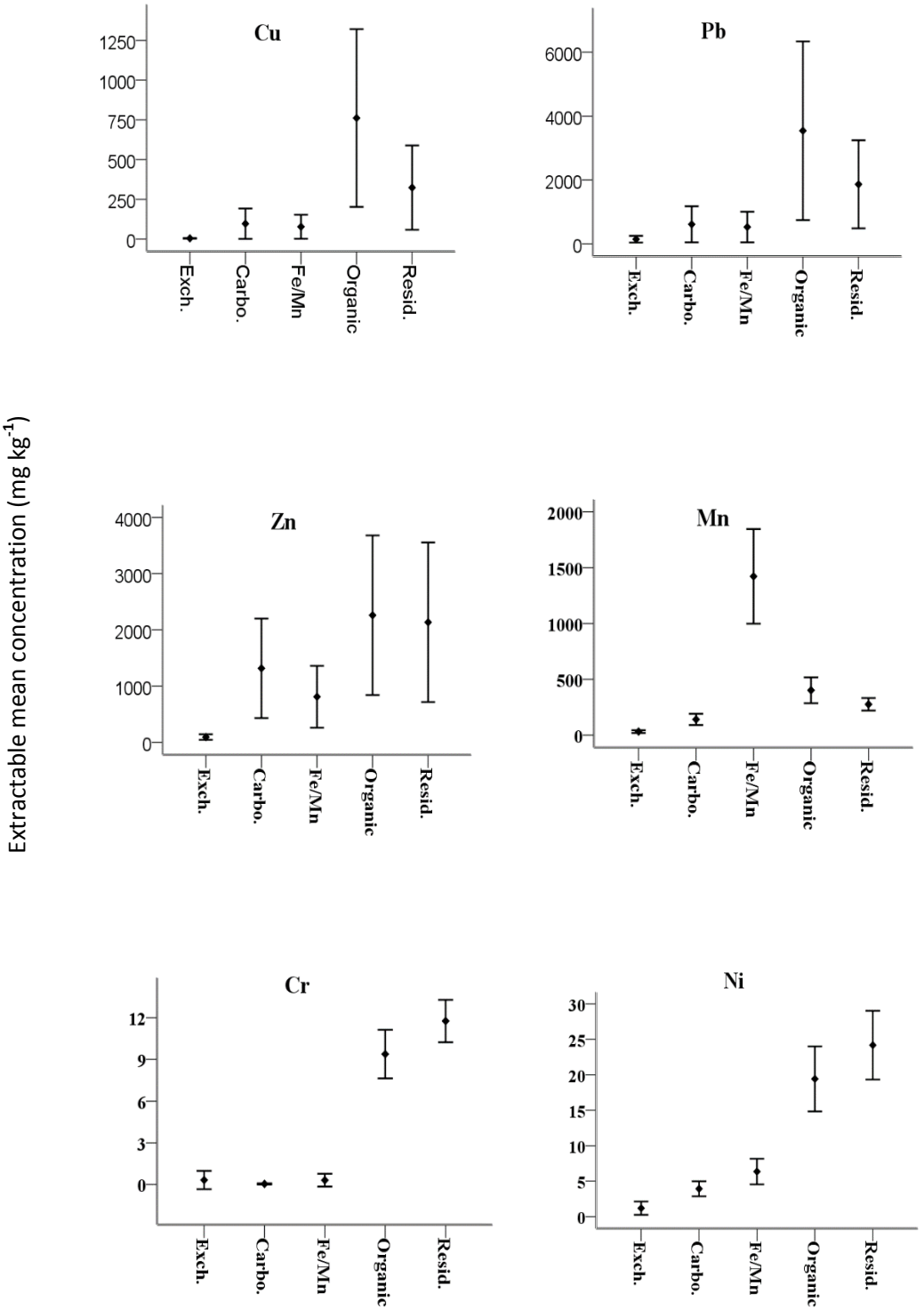


Figure 7.13: Showing mean concentration of the sequential extraction of metals being studied assigned to different soil phases (n=37) – continues next page.

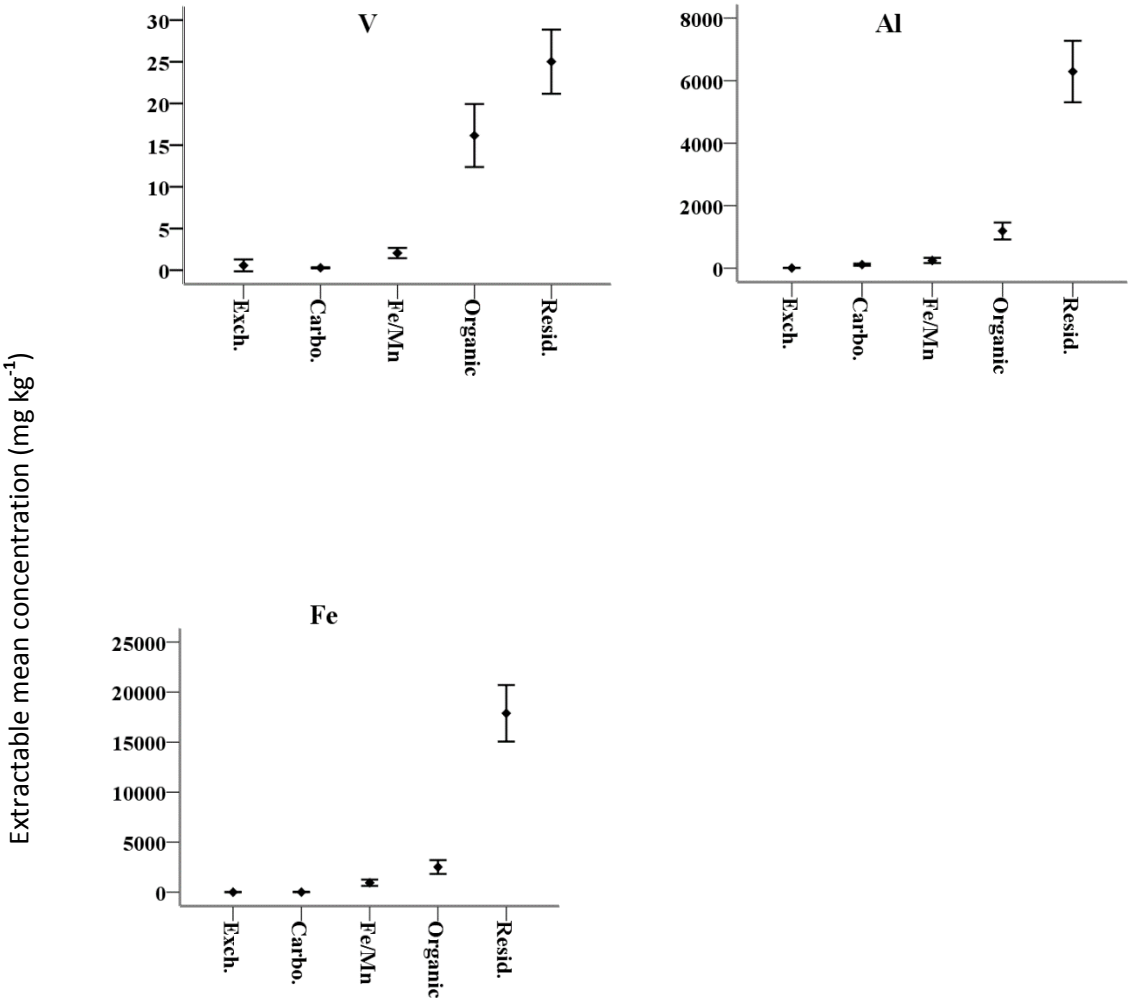


Figure 7.13: (Continued): Showing mean concentration for the sequential extraction of metals being studied assigned to different soil phases (n=37).

However, the V extracted from the residual fraction was higher than that extracted in the case of Ni (Figure 7.12). Similar to the case of Ni, vanadium is present the minimum amount assigned to the exchangeable phase with the exception of ES1 where there is more V associated than the carbonate phase.

Generally, Fe and Al are mostly associated with the residual phase, and show a similar trend in terms of the amount being assigned to the five metal phases. The extraction figures for Fe and Al illustrate that there is more iron and aluminium assigned to the residual phase than all of the other fractions combined and for all of

the samples. Figure 7.12 shows that there is no Fe available in either the exchangeable or carbonate phases. Unlike Fe, Al was extracted from the carbonate fraction for the majority of the samples and reached more than 7% of the total extractable in sample ES32. All of the samples had a substantial amount of iron and aluminium assigned to the organic phase with the exception of samples ES5 and ES7 for Fe and samples ES8 and ES11 for Al (Figure 7.12).

7.6.3. Discussion

The sequential extraction results demonstrate that aluminium and iron are dominated by the residual fraction, which accounts for more than 80% of the total metal present for the majority of the samples (Figure 7.12). This suggests that the mobility of these two metals is relatively low. However, a noticeable amount of Al and Fe is associated with the organic matter (i.e. oxidisible phase) for most of the soil samples studied, indicating that clay and organic matter play an important role for the binding of these two metals (Fatianos and Lorantuo, 2004; *Li et al.,* 2007). As a result, this considerable amount available in the oxidisible phase can be remobilised under oxic conditions causing harm to the surrounding environment. In addition, with the exception of a few samples, (figure 7.12) some Fe and Al was extracted from the Fe/ Mn fraction (i.e. reducible), illustrating the presence of oxides and hydroxides of these two elements. This may be due to the low buffering capacity that collected soils have. Therefore, the chemical reagent will be able to reduce the pH enough to cause partial dissolution of these metal oxides, and thereby they can be released into the solution due to the fact that dissolution of these elements is being pH dependent (Byrne and Luo, 2000).

Copper is mostly extracted from the organic fraction followed by the residual phase, with Cu being associated approximately equally to these two phases in samples ES12, ES13, ES14, ES17, ES18, ES27, and ES30 (Figure 7.12). The presence of a higher amount of Cu extracted from the organic matter and residual fractions compared with the other phases indicates that this element was not been completely dissolved by the reagent used during the initial steps of extraction and, subsequently, stronger chemical reagents in next step of the extraction had more effect in terms of dissolving the element from this phase, and thereby it was released into the solution. Similar results have been reported by others, for example Wn *et al.* (2016) and Pejman *et al.* (2017). The significant percentage of Cu being extracted from the residual and organic matter compared to the other fractions suggests that this element had low mobility in the study area. In addition, the association of Cu mainly with the oxidisible phase (i.e. organic matter fraction) is likely to indicate that there is a link with the organic matter constituent or present in the form of sulphide minerals (Cao *et al*., 2003). The latter scenario is more likely because, as previously mentioned, this area has been mined for a long period to extract sulphide minerals (refer to mineralization section in chap. 2), with chalcopyrite and chalcocite being possible sources of copper. It is worth mentioning that, however, in the case of samples ES1, ES7, ES9, ES15, ES21, ES22, ES23, ES32, and ES 34, a substantial amount of Cu was extracted from both the carbonate and Fe/Mn fractions, with samples ES9 and ES21 having nearly 50% of the total metal extracted (Figure 7.12). This suggests that, as indicated previously, oxides of iron, manganese and aluminium, to some extent, act to bind Cu to the surface of soil particles. Therefore, Cu may be released from these oxides into the solution when undertaking sequential extraction process. Furthermore, it should be noted that Cu has also been found to

have an amount been extracted from easily and exchangeable phase in the case of the sample ES1 having nearly 5%. This may indicate that Cu is more prone to release from this site due to acidification effect while performing sequential extraction.

In the case of lead and zinc, from Figure 7.12 it can be seen that these two elements have a similar pattern of fractionation to that of Cu. This is consistent with the results already obtained from the principal component analysis (PCA), which showed that these elements have the same source and therefore are likely to behave similarly. However, in the case of zinc, a noticeable amount was extracted and associated with the exchangeable phase for the majority of the soil samples. This suggests that this element is more mobile and susceptible to dissolution due to acidification compared to Cu and Pb. This is consistent with results obtained elsewhere, for example by Zheng *et al.* (2016), who found that zinc was associated with the soluble fraction (i.e. exchangeable fraction) in all of the samples studied. As a result, Zn should be given special consideration at this site, due to its availability in the exchangeable phase, which contains metals that are mobilised and can become easily available to plants and other living organisms (Pandey and Bhattacharge, 2016), which in turn may pose a threat to the food chain because of greater mobility.

With regard to Mn, this element has the highest extractable level in the Fe/Mn fraction (reducible phase), accounting for more than 60% for the majority of the soil samples studied. This might indicate that Mn occurs as oxides/ hydroxides in the soil.

In addition, the presence of manganese mainly in this fraction, which is resistant to chemical attach, suggests the crystalline form of Mn that can be extracted by a

strong reagent like hydroxylamine hydrochloride (Hudson-Edward, 2000). Therefore, the results show that Mn occurs mainly as a very crystalline form. It is worth mentioning that Mn is also associated with the easily soluble and exchangeable fraction for the majority of the samples. This may suggest that a little acidification on the site can release more of the manganese and thereby metals bound to its oxides.

In the case of chromium, nickel, and vanadium, from Figure 7.12 it can be seen that these metals exhibit similar fractionation behaviour with a substantial amount being associated with the organic and residual fractions. Similar findings were reported elsewhere, for instance by Marco *et al.* (2016) and Zheng *et al*. (2016). All three trace metals show a high concentration extracted from the organic matter (i.e. oxidisible fraction), which is highly resistant to chemical attach. Such an association indicates that organic matter and sulphides are most likely to play an important role for binding these elements. According to Hueta- Diaz *et al.* (1998), sulphides act as a significant sorbent for heavy metal. This seems to be the scenario at the study area because, as mentioned before, the study area has a legacy of mining for sulphide minerals such as galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and chalcocite (Cu_2S) (refer to chap. 2, mineralisation section). As a consequence, these metals have a relatively low mobility due to the higher amounts extracted from the residual fraction, which is well known to be the most stable fraction. However, in the case of Ni, and V, there are some cases in which a remarkable amount was extracted from the exchangeable phase, for instance samples ES1, ES2, ES16, and ES36 in the case of Ni and samples ES1, ES12, and ES28 in the case of V.

This is probably due to the fact that acetic acid causes the pH of the solution to drop, resulting in the release of both chromium and vanadium from the soil samples

mentioned above. Therefore, it can be concluded that Ni and V are likely to be susceptible to the acidification of the soil in the study area.

Finally, it is worthwhile mentioning that all of the metals studied have a substantial amount associated with the organic matter, indicating that organic matter and sulphides play an important role in the fractionation of the metals studied. This has been confirmed by Calmano *et al.* (1993), who highlighted the importance of sulphides for binding heavy metals, which can be easily released into the surrounding environment when sulphides are oxidised to sulphates.

7.7. Buffering capacity and acidification

One of the most important characteristics of the soil is its buffering capacity, which has a substantial effect on the release of pollutants bound to the surface of soil particles. According to Elzahabi (1999), decreasing the pH of the soil is most likely to lead to the dissolution of soil components (e.g. carbonate and metal oxides) which are responsible for binding contaminants to the soil surface. As a consequence, pollutants that bound to these components are most likely to be released into the soil solution. Therefore, pH changes in the soil have an important influence on the solubility of heavy metals that are bound to the soil particles.

The durability of soils in regard to changes in pH (i.e. acidification) or buffering capacity depends on the chemical composition, with calcium, carbonate, and Al, Mn, and Fe oxides being the key factors that affect the buffering capacity of the soil (Christensen, 1998; Singh *et al.,* 2003).

The major chemical reactions that govern soil acidification are (Calmano *et al.,* 1993):

$$CaCO_3 + 2H^+ = Ca^{+2} + H_2O + CO_2$$

$Al_2O_3 + 6H^+ = 2Al^{+3} + 3H_2O$

$Fe_2O_3 + 6H^+ = 2Fe^{+3} + 3H_2O$

When studying and appraising environmental pollution caused by heavy metals in soil and sediments, evaluation of the buffering capacity is of great interest because it helps to understand the extent to which potential toxic heavy metals can be released into the surrounding environment as a consequence of acidification. Therefore, the buffering capacity for the soils studied was measured using the procedure explained in Rowell (1994). According to this method, a specific amount of acid is added to the samples in many stages and at each step the reduction in the pH reading is recorded until a stable reading is achieved. Figure (7.14) shows the buffering capacity of the soil samples collected from the study area.

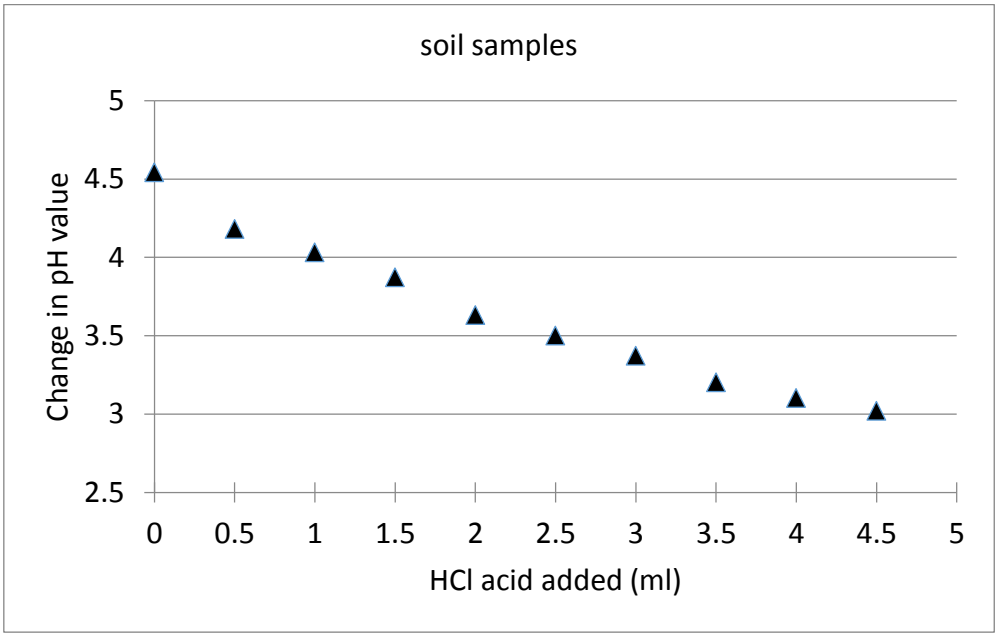


Figure 7.14: Buffering capacity of the topsoils collected from study area.

It is obvious from the figure 7.14 that there was an average drop in pH of approximately 1.2 points after 3.5 ml of HCl (0.1 M) had been added, and then the reduction level reached the minimum. Such a reduction may indicate that acidification can result in the release of metals bound to the soil surface of the samples studied.

Another important factor that plays a significant role in the interaction between heavy metals and soil components is the redox conditions. The redox potential for all of the collected soil samples was measured (refer to chapter 3 for procedure used) and the results are shown in figure (7.15). It can be seen that the highest redox potential was demonstrated by sample ES26, for which 218mV was recorded. However, the lowest value recorded was -264mV for sample ES34. Therefore, the data indicate that the study area exhibits both oxic and anoxic conditions. The effect of this factor is crucial in the case of sulphide minerals, which usually occur and are available under reducing conditions. These can be oxidised and consequently lead to the release of contaminants bound to (Stephens *et al*., 2001; Forster, 1993). As a result, the oxidation of sulphide minerals may result in the acidification of the system and this becomes more important as the pH drops to 2-3 (Calmano *et al.,* 1991; Foster, 1993).

The process of sulphide mineral oxidation and consequent acidification has been described by Jenkins *et al.* (2000), using the following reaction:

$MS_{(s)} + 2O_2 + \rightarrow M^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$

Where: MS are Sulphide minerals

In addition, these authors highlight the oxidation of pyrite (marcasite) as an example that occurs due to acid mine drainage (AMD) (refer to reactions in section 5.2.3.).

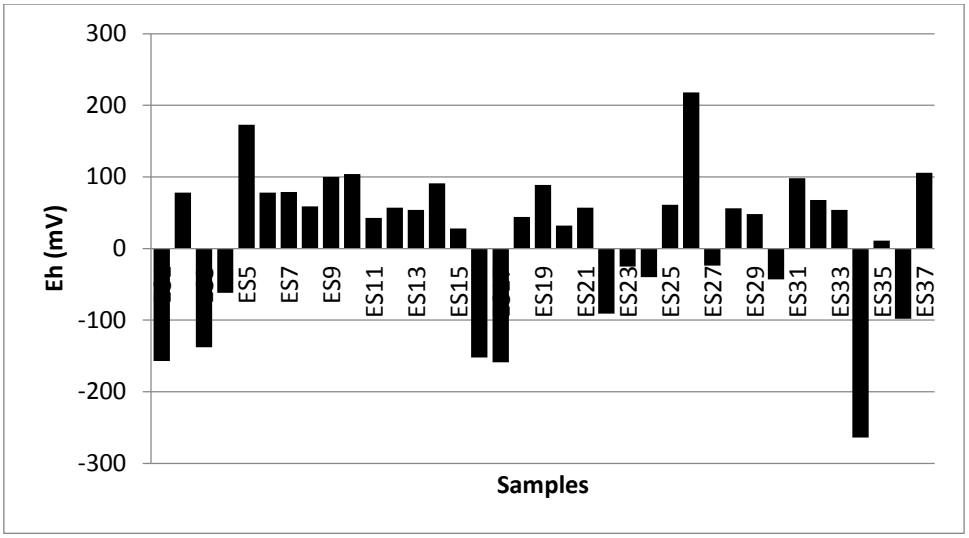


Figure 7.15: Redox potential for the collected samples at the study area.

From the above reaction, it can be seen that in some situations of oxidised sulphides, iron hydroxides are formed, and thereby may act as sorbents for heavy metals. This has been demonstrated and mentioned previously in the principal component analysis (PCA) in which Fe and Al oxides play a significant role in binding pollutants. However, when the environment is changed from oxidising (an oxic) to reducing conditions, an adverse effect will happen. As a consequence, metal oxides undergo dissolution, and hence releasing trace metals bound to (Chuan et al. 1996). This is most likely the case in our study area because, as discussed previously, this area was mined to extract copper, lead and zinc from sulphide ores such as chalcopyrite, galena, and sphalerite (refer to chapter 2 – mineralisation section).

7.7.1. Specific soil components responsible for the binding of the heavy metals examined in the soils from the study area (sequential extraction and PCA results combined)

A change in the pH and redox conditions of soils will influence heavy metals that bind to their particles. As discussed previously in the leaching test section, different

metals show various leachable amounts, indicating that different processes may control how these metals reacts with specific components of the soil, such as organic matter contents metal oxides. In addition, it has been seen, when fractionation of some major and trace elements was discussed, that different metals have associated amounts extracted that are quite different between various soil phases. This may indicate that individual elements are controlled by the acidity and redox conditions of the system. As a consequence, elements associate differently in the various soil phases.

As it has been discussed earlier, from the principal component analysis results, it can be seen that there are three components that are responsible for the binding of the seven metals being studied (i.e. Cu, Pb, Zn, Mn, Cr, Ni, and V). The first component consists mainly of Al and Fe oxides along with organic matter, although the levels recorded for organic matter was low compared to those for iron and Aluminium oxides. In addition, the presence of V, Cr, and Ni strongly associated with this component indicates that Fe and Al oxides and organic matter play a significant role in binding these metals.

The second component includes clay and silt that are strongly linked with this component, which also has Ni associated with. This may indicate that clay and silt have an important role for binding Ni to the soil particles (Table 7.4).

The third component comprises Cu, Pb, and Zn that have been correlated strongly with this component, which also has organic matter being strongly associated with it. This most likely to indicate that organic matter contents are responsible for binding these elements to the soils of the study area. However, the three aforementioned components do not show any role for binding Mn, which was found to be associated with the fourth component in which organic matter and cation exchange capacity

(CEC) are also found to be associated with. Therefore, it can be concluded that Mn is more likely to be bound to the soil particles by the soil organic matter contents, which has high cation exchange capacity amount.

7.7.2. How changing the pH and redox conditions can affect the binding and releasing behaviour of the metals being examined at the study area

Understanding the results have been obtained so far from the leaching test, principal component analysis (PCA), and sequential extraction data, it is possible to draw some conclusions and make some predictions with regard to the possible release of the heavy metals studied when the surrounding environmental conditions change. To this end, in the following section, the effects of pH change (acidification) and changes in redox conditions will be discussed, supposing that there is a drop in pH of 2 points in the study area so that the potential behaviour of the metals being tested can be predicted.

7.7.2.1. Effects of acidification

Many researchers (e.g. Esnaola and Millan (1998) and Chuan et al. (1996)) have pointed out that pH is the significant factor that controls solubility and mobility of heavy metals. In addition, according to Alloway (1995), hydrogen ions (H^+) have a strong affinity to the negatively charged surfaces and displace most other cations; hence it plays an important role in binding metals to the surface of clay minerals and organic materials (Alloway, 1995). As a consequence, in humid climates, due to the acidic conditions, an extra hydrogen ions will be added, which try to bind to the sites of negatively charged clay and organic matter; therefore, weakly bonded metals will be released and consequently their concentration will be increased in the solution system (Brady, 1984).

Generally, in acidic conditions, the majority of metals tend to be mobilised and accumulate strongly in alkaline conditions (Plant and Raiswell, 1983). For instance, Rending and Taylor (1989) found that higher concentrations of copper, zinc and nickel were soluble in acidic conditions in comparison with alkaline conditions.

To examine the process occur as a result of acidification, the buffering capacity of the soil studied was measured (refer to Figure 7.14), and it can be seen that the study area has a relatively low buffering capacity; the pH dropped from 4.4 to 3 after the addition of 4ml acid. As humic substances have complexing ability due to their 'multi-ligand' nature (Buffle, 1988), it is expected that some of the metals would be released from the functional groups of the organic matter into the soil solution when the soil acidified due to the competition of hydrogen ions for the complexing sites, and hence heavy metals would be released (Fig. 7.16). However, not all of the metals will undergo dissolution and consequent release from the organic matter present. This seems likely to be low under slight acidification, and this is quite clear when looking at the sequential extraction results. As discussed previously in regard to the sequential extraction, the minimal association found for Cu, Pb, Zn, Mn, and Ni with the exchangeable fraction suggests that they are most likely to be released into the soil solution during extraction.

Oxides of Fe and Al are strongly associated with component 1 (refer to PCA analysis-section 7.5), which also has Cr, Ni, and V associated with. This may suggest that the acidification of the soil has a substantial role in releasing these metals from the oxides mentioned above. Kedziorek and Bourg (1996) pointed out that metals would begin to release from oxides of iron when the pH falls below 5.4. Likewise, the same process is thought to occur at the study area, and hence a noticeable amount of heavy metals will be released from this source.

From the principal component analysis results, clay and silt correlated strongly with component 2, which also has Ni correlated with it. In addition, from sequential analysis results, Ni has a remarkable amount extracted from the easily exchangeable phase indicating that less acidification of the site will release nickel from this component. As a result, at the study area clay and silt represent an important source for Ni.

Overall, it can be conclude that the effect of acidification is very important at the study area, and a fall in pH of 2 point as mentioned earlier can cause a significant release of the metals being examined (Fig. 7.16).

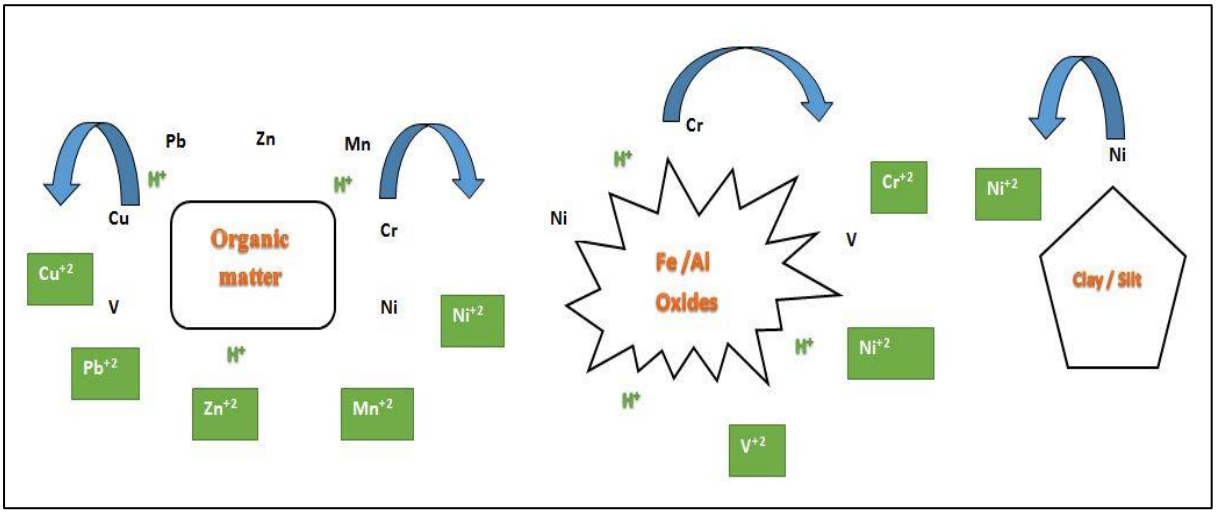


Figure 7.16: Showing the process happening as a consequence of acidification of the collected soil samples.

7.7.2.2. Effects of changing of redox conditions from oxidising to reducing

Potential redox of the samples being studied has been measured, and the results indicate that the redox conditions at the study area are dominated by both oxic and anoxic conditions (Figure 7.15). Therefore, it should be taken into account that any

changes in the redox conditions may affect the leachability of the heavy metals at the study area.

To discuss this effect, it will be supposed that the condition would change to reducing without a change in the acidity (pH).

According to Charlatchka and Cambier (2000), the main effect that occurs during a change in the redox conditions from oxidising to reducing is the reduction of oxides of iron and aluminium. From the principal component analysis (PCA) results, it has been discussed earlier that oxides of Fe and Al are strongly associated with component 1 (Table 7.4), which also has Cr, Ni, and V associated with it. Consequently, under a change to reducing conditions, it is most likely that these oxides would be dissolved, and hence releasing metals are bound to them. As a result, it would be expected that Cr, Ni, and V will release to the soil solution (Fig. 7.17).

Another key influence resulting from a change to reducing conditions is that, the mobility of iron would be enhanced from component 1 due to the reduction of iron from Fe^{+3} oxidation state to Fe^{2+}, which is more mobile under reduced conditions (Schwertamann, 1991). Unlike iron, the mobility of chromium is most likely to be reduced due to Cr being changed from the Cr^{+6} oxidation state to Cr^{+3}, which has lesser toxicity and mobility compared to Cr^{+6} (McGrath and Smith, 1995).

This is confirmed by the results of the sequential extraction (Figure 7.12), where no chromium was extracted from the reducible phase, except for sample ES5, in which chromium accounted for about 40% of the total metal extractable. This may be attributed to the pH value being low when performing the extraction, which may have influenced the amount of chromium extracted.

Finally, it would be worth noting that under a change to a reducing condition, metals are more likely to precipitate in the form of sulphide minerals, and hence decreasing their mobility (Maes *et al.,* 2003). In addition, as has been previously mentioned the study area was used to mine sulphide minerals (refer to chapter 2, mineralisation section), sulphide waste may play a significant role in binding metals and especially Cu, Pb, and Zn and thereby decreasing the mobility of these elements. Clamano *et al.* (1993) highlighted the importance of sulphides for binding metals in anoxic (reducing) conditions.

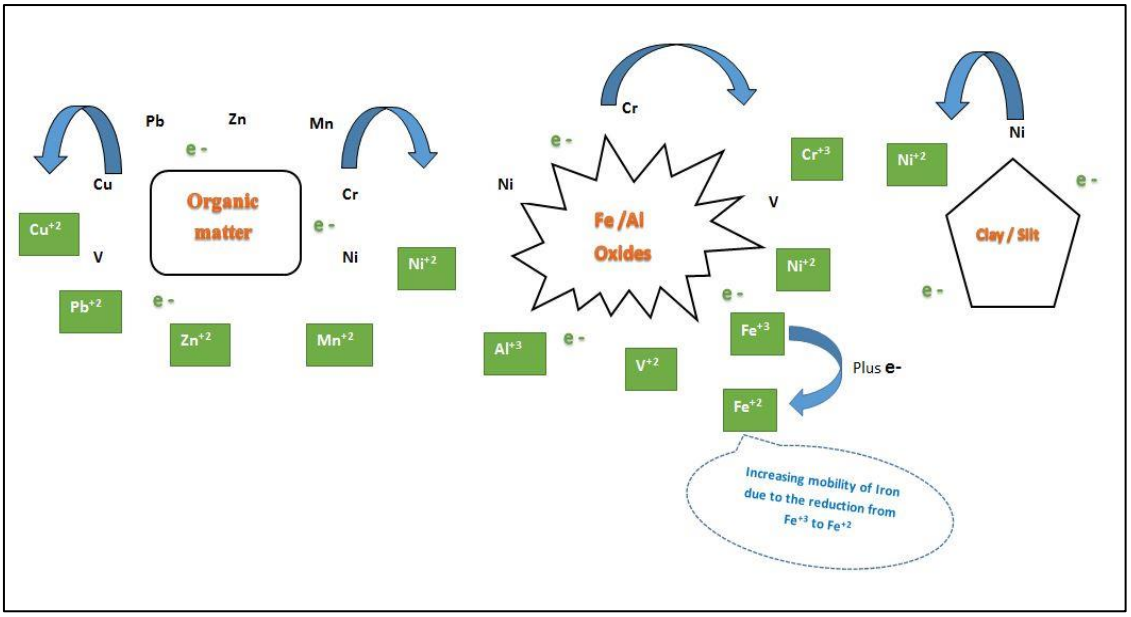


Figure 7.17: Showing the process happening as a consequence of changing the redox potential to reduction condition for the collected soil samples.

7.7.2.3. Effects of changing redox conditions from reducing to oxidising

The study area, as has been mentioned before, was used for extracting metals from sulphide minerals (refer to mineralisation section in chapter 2). Therefore, it would be worth investigating the implications of changing the redox conditions of the soils from anoxic to oxic conditions. This is due to the fact that approximately half of the

samples studied were found to be in reducing conditions (anoxic) (Figure 7.15). According to Calmano et al. (1993), sulphides play an important role for binding metals under reducing conditions where they are usually found, and hence changing redox conditions to oxidising may lead to a release of bound metals.

Soils found in reducing conditions would be susceptible to a remarkable chemical alteration when they are exposed to plenty of oxygen (oxidation). As a result, Fe would be oxidised from the Fe^{+2} to the Fe^{+3} oxidation state, thereby reducing its mobility. This would be followed by the acidification of the system (Figure 7.18 – equation 2).

From the sequential extraction results, it can be seen that all of the heavy metals have a substantial amount associated with the oxidisible phase (organic and sulphide) (Figure 7.12). Therefore, due to the acidification mentioned above, these metals will undergo dissolution and be released into the solution (figure 7.18). However, some of the released metals will be re-adsorbed and precipitated on the iron oxides that form (Calmano *et al.,* 1993). In addition, the authors also point out that the oxidation of sulphides will cause a substantial reduction in pH, which may fall to a pH of 2 due to the forming of the sulphate ion SO_4^{-2} and, hence, the production of sulphuric acid. This greater fall in the pH of the system will influence the solubility of the heavy metals, thereby enhancing their release from Fe/Al oxides and organic matter.

This scenario is more likely to happen in the study area due to anthropogenic activities, such as ploughing whilst farming the land for agricultural purposes, which may lead to the oxidation of the soil upon exposure to the atmospheric oxygen, resulting in heavy metals being released into the surrounding environment, as discussed above.

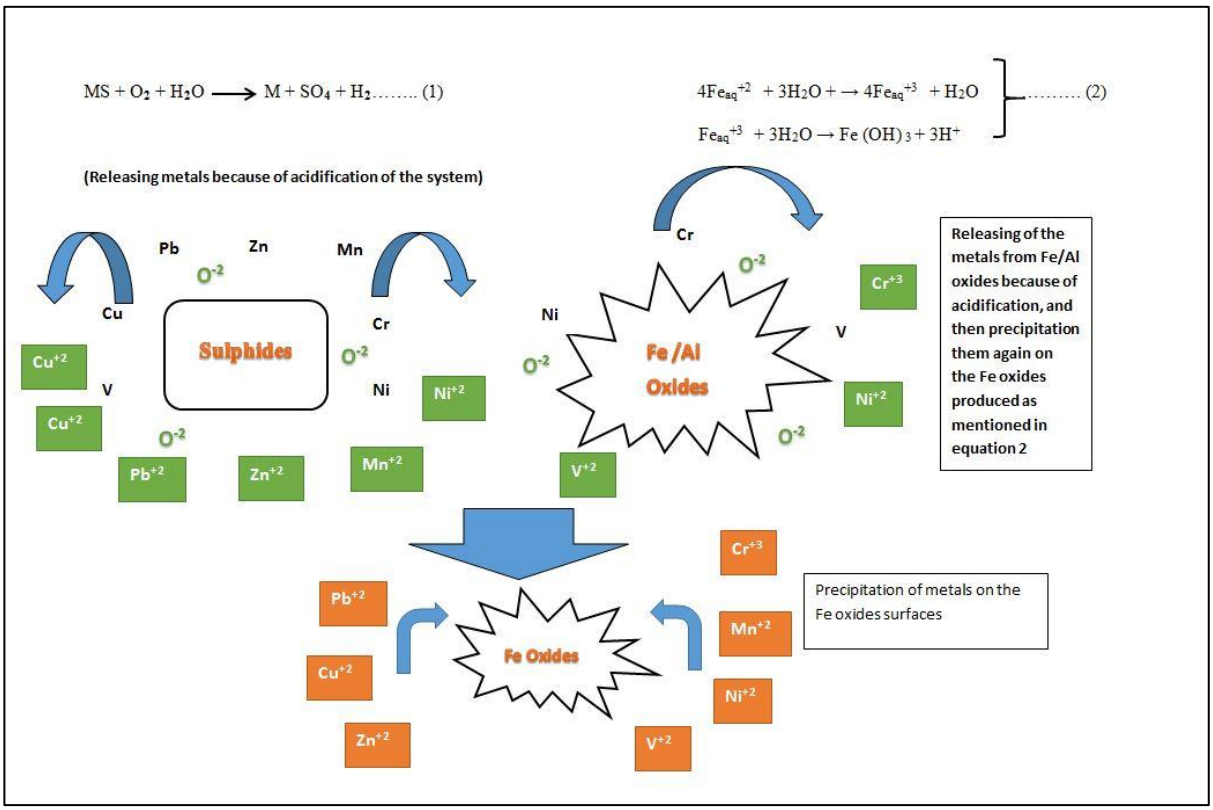


Figure 7.18: Showing the process happening as a consequence of changing the redox potential to oxidation condition for the collected soil samples.

7.8. Summary

The speciation, leachability, and acidification of the selected heavy metals and some major elements from the topsoil samples were characterised. In terms of speciation, a five-step speciation approach was applied and the results indicate that Cu, Pb, and Zn are found to be mainly associated with the organic phase, whilst Cr, Ni, V, Al and Fe are mainly associated with the residual fraction. Regarding the leachability, the highest leachability among the metals studied was demonstrated by Zn, whereas the lowest leachability was exhibited by Cr. Generally, all of the metals demonstrated a low leachable amount from the soil samples in the study area.

The principal component analysis (PCA) technique was applied to indicate the main soil specific factors that bind pollutants to soil surfaces. The results demonstrate that

Ni is bound by the clay and silt granulometric range, Cr, Ni, and V are bound by oxides of Fe/Al, and Cu, Pb, and Zn are bound by the organic matter content of the soil.

The acidification of the soil in the study area was tested, and the findings show that the process of acidification is likely to result in the release of Ni from the clay and silt fractions, Cr, Ni, and V from the oxides of Fe/Al, and Cu, Pb and Zn from the organic matter content.

The consequences of changing the redox potential from oxidising to reducing conditions were examined. Such a change is more likely to result in the metals studied being released from soil specific components. In addition, the mobility of iron is increased due to the reduction of iron Fe^{+3} oxidation state to the Fe^{+2} oxidation state, which is more mobile and toxic than the former oxidation state.

Finally, the effects of changing the redox potential from reducing to oxidising were also investigated. The consequence of this process might be the release of the studied metals from the sulphides, because oxidising of the sulphides is the most significant geochemical alteration that can happen in the study area, and hence the system is acidified. However, some of the metals released might undergo re-adsorption by the iron oxides produced during the process.

Chapter eight: Conclusions

8.1. Introduction

In this chapter the key findings will be summarised in line with the aims and objectives which have been set out in chapter two of the current research. Then, the limitations of the research will be explained. This will be followed by the possible implications and recommendations for land owners for different land uses. Finally, recommendations for further work will also be suggested.

The aims of this research, as has been mentioned earlier, are to evaluate whether there are high levels of some selected heavy metal (Cu, Pb, Zn, Mn, Cr, Ni, and V) in the topsoil and floodplain samples at the study area (Ecton Hill) and, hence, to determine the possible sources for such elevated levels, and to investigate the degree of heavy metal pollution and how this might influence different land uses. In addition, to indicate whether the selected heavy metals are bioavailable and what are the soil specific factors that control fractionation, mobility and bioavailability of metals being studied.

To achieve these aims, topsoil and floodplain samples have been collected from the study area and analysed for their total, bioavailable fractions. In addition, soil pH, Eh, organic matter content, grain size distribution are also analysed to illustrate their effects on the leachability and fractionation of metals studied.

On the basis of the aims and objectives of this study which are set out in chapter two, the following objectives have been achieved:

1. The spatial distribution maps of heavy metals concentrations over the study area have been illustrated.

2. Heavy metals contamination level has been appraised using both geoaccumulation indexes (I_{geo}) and enrichment factor (EF) on the basis of the local background concentrations (limestone). In addition, heavy metal concentrations have been evaluated for different land uses on the base of both ICRCL and CLEA soil guideline values.
3. The bioavailable fractions of metals studied in the collected soil and flood plain samples have been determined using Ethylene Diamine Tetra acidic Acid (EDTA) approach.
4. The relationship between bioavailable fraction of heavy metals and soil specific factors (i.e. organic matter content, grain size and PH) has been examined using principle component analysis (PCA) approach.
5. Heavy metals concentrations along a cross section over the River Manifold floodplain soils have been examined, with a distance interval of (5m) from the river channel.
6. Leachability, speciation and buffering capacity of heavy metals being studied are also examined, and hence soil specific factors responsible for binding heavy metals to the soil surfaces were specified.
7. Finally, conceptual models, which illustrate the consequences of changes of pH and redox potential (Eh) on binding and releasing of metals studied, have been constructed.

It is worth noting that the unique contribution that the current research makes to knowledge is providing a conceptual model which describes the partitioning and leachability behaviour of metals being studied when pH and redox potential are changed. This conceptual model has not been done before in this area. In addition, a

new approach for heavy metal contamination assessment has been utilised at the study area to indicate the potential ecological risk via enrichment factor (EF).

8.2. Summary of findings

The main findings of this research can be summarised as follows:

1. In relation to the spatial distribution maps of Cu, Pb, and Zn using the GIS approach, it can be seen that elevated concentrations were recorded close to the mining waste sites (refer to spatial distribution maps in chap. 4), suggesting a possible anthropogenic source of these metals. In addition, all of the metals studied, except for Ni and V, were found to have concentrations higher than that the local lithology background (limestone), indicating that the former mining activities are more likely to be responsible for such elevated levels, along with natural sources (genogenic) for Ni and V.
2. Regarding the degree of contamination, the levels of contamination were evaluated using geoaccumulation indexes (I_{geo}), and the results indicate that Pb has the highest amount of contamination extremely contaminated (class 6) in both the floodplain and soil samples. This was followed by Zn and Cu. However, other studied metals (Mn, Cr, Ni, and V) were shown to have a contamination level ranging between uncontaminated/moderately contaminated (class 1) and moderately contaminated/ strongly contaminated (class 3). (refer to chapter 4).

3. With regard to the ecological risk assessment using the enrichment factor (EF), the enrichment factor (EF) for Pb was the highest among the studied metals followed by Zn and Cu. The potential environmental risk of Pb, Cu, and Zn was found to be the highest in both the floodplain and soil samples,

and ranged from significant enrichment (group 3) in floodplain samples to extremely high enrichment in the soil samples. However, V, Cr, Mn, and Ni were associated as group 1 (deficiency to minimal enrichment) in both floodplain and soil samples, except Cr which was found to have a potential environmental risk of significant enrichment (group 3).

4. Heavy metal concentrations have been assessed for different land uses by comparing with the UK guideline values, and results indicate that on the basis of the ICRCL trigger values recommended for different land uses, Cu, Pb and Zn average values exceed the levels for all the purposes for both soil and floodplain samples, except for floodplain samples for which Cu, Pb and Zn are recommended for the grazing livestock, park and recreational purposes. However, when comparing with CLEA SGVs levels, Cr and Pb have shown the same usages in both soil and floodplain samples, except Pb which shows level suitable for commercial/industrial purpose in the case of the floodplain samples.

5. A fairly strong positive correlation between the two methods (i.e. geoaccumulation index (I_{geo}) and enrichment factor (EF) was found, with a correlation coefficient of $R^2 = 0.7617$, indicating that both methods are reliable for such an assessment, with acceptable results being recorded.

6. Due to the use of the area for agricultural purposes and stock rearing, the bioavailability fractions of the metals studied were calculated using the (0.01 M EDTA) method as this will help to predict the possible risks that pollutants can pose to human health. The results indicate that Cu, Pb, and Zn have the

highest bioavailable fractions with their bioavailable amounts decreasing in the following order:

Soil samples > floodplain samples

7. The high levels of bioavailable fractions for Cu, Pb, and Zn are most likely to be due to the former anthropogenic activities in the area.

8. The bioavailable fractions (i.e. EDTA metals extraction) for the metals studied were assessed by comparing them with the national mean values for England and Wales. The findings demonstrate that the amount of EDTA metal extractable for all of the selected metals from the soil samples exceeded the national average for England and Wales, except for Mn and Ni. The EDTA values of Cu, Pb, and Zn in soil samples were 3.35, 7.47, and 10.72 times the national average amount, respectively. However, the bioavailable fractions for the floodplain were lower than the national mean values, except for Cu and Zn (refer to chapter 5).

9. The relationship between the bioavailable fractions and the total heavy metals was examined; the results indicate that there is a positive correlation between the EDTA metal fractions and their total concentrations for Cu, Pb, and Mn for both floodplain and soil samples, except for Pb and Mn in the case of floodplain samples.

10. The principle component analysis (PCA) approach was applied to find the possible associations between the bioavailable fractions of the examined heavy metals and the physico-chemical properties of the soil (i.e. organic matter content, pH values, and different granulometric classes. From the

analysis, four components were extracted, which explain 70.2% and 96.6% of the total variance for the soil and floodplain samples, respectively. The results show that there are different association forms between the bioavailable fractions of the metals studied and soil specific parameters, with the predominant influence of organic matter and pH (refer to chapter 5).

11. The distribution of the examined metals (Cu, Pb, Zn, Mn, Cr, Ni, and V) across a section through a selected floodplain, with an interval of 5m from the channel of the Manifold River, was investigated (refer to chapter 6). The results indicate that there are two patterns of distribution from the channel. The first pattern included Cu, Pb, Zn, and Mn. These metals show a similar trend of distribution through the floodplain with the general levels increasing away from the river channel. However, the second pattern of distribution includes Cr, Ni, and V, which demonstrate approximately a stable form of distribution from the river channel. Generally, the majority of the metals show high concentrations close to the river bank within the zone of 20m from the river channel.

12. Regression analysis was applied to find out whether there was a relationship between the concentrations of the studied metals and the distance from the river channel across the floodplain soils (refer to Figure 6.2). Different regression equations were used, including polynomial, potential, linear and logarithmic, and the results show that Mn has a best fit regression equation with the highest R^2 amount of 0.8253, whereas Ni demonstrates the lowest R^2 value of 0.0856. For all of the investigated elements in the floodplain soils,

the R^2 amount showed a general reduction trend as follows: Mn > Zn > Pb > V > Cu > Cr > Ni.

13. The correlation and association between the studied heavy metals in the floodplain was examined using Spearman rank correlation coefficients. Such a relationship gives an insight into how metals relate together in the system of interest because metals belonging to the same source behave similarly to some extent. The results demonstrate that Cu, Pb, Zn are associated with a fairly strong correlation, whilst a weak correlation was shown between Cr, Ni, and V, indicating that Cu, Pb, Zn are most likely to be derived from the same source, which might be attributed to the former mining operations in the study area.

14. The correlation of the metals studied with organic matter content and soil pH for the floodplain was determined. The results indicate that Cu, Pb, Zn, and Mn are correlated positively with the pH value, with Zn showing a strong positive correlation at a significance level of 0.01. Regarding the organic matter content, Cu, Pb, Zn, and Mn showed a positive association with organic matter content. (refer to chapter 6).

15. In the floodplain soils, the metals studied correlated with the main three granulometric classes (i.e. clay, silt, and sand). The results demonstrate that all of the studied heavy metals are correlated positively with both the clay and silt fractions, except for Cr, which has a negative association, with the highest association being for manganese, vanadium, and Zinc. This may indicate the role of clay in adsorbing these metals.

16. The speciation, leachability, and acidification of the selected heavy metals and some major elements from the topsoil samples were characterised. In terms of speciation, a five-steps speciation approach was applied and the results indicate that Cu, Pb, and Zn are found to be mainly associated with the organic phase, whilst Cr, Ni, V, Al and Fe are mainly associated with the residual fraction. Regarding the leachability, the highest leachability among the metals studied was demonstrated by Zn, whereas the lowest leachability was exhibited by Cr (refer to chapter 7). Generally, all of the metals demonstrated a low leachable amount from the soil samples in the study area.

17. The principal component analysis (PCA) technique was applied to indicate the main soil specific factors that bind pollutants to soil surfaces. The results demonstrate that Ni is bound by the clay and silt granulometric range, Cr, Ni, and V are bound by oxides of Fe/Al, and Cu, Pb, and Zn are bound by the organic matter content of the soil (refer to section 7.5in chapter 7).

18. The buffering capacity for all of the topsoil samples collected was examined on the basis of the amount of HCl added, and the results indicate that the study area is dominated by both oxic and anoxic conditions (refer to Figure 7.15 in section 7).

19. The acidification of the soil in the study area was tested, and the findings show that the process of acidification is likely to result in the release of Ni from the clay and silt fractions, Cr, Ni, and V from the oxides of Fe/Al, and Cu, Pb and Zn from the organic matter content (refer to Figure 7.16).

20. The consequences of changing the redox potential from oxidising to reducing conditions were examined. Such a change is more likely to result in the metals studied being released from soil specific components, as shown in Figure 7.17. In addition, the mobility of iron is increased due to the reduction of iron from the Fe^{+3} form to the Fe^{+2} form, which is more mobile and toxic than the former oxidation state.

21. The effects of changing the redox potential from reducing to oxidising were also investigated. The consequence of this process might be the release of the studied metals from the sulphides, because oxidising of the sulphides is the most significant geochemical alteration that can happen in the study area, and hence the system is acidified (refer to chemical equations in Figure 7.18). However, some of the metals released might undergo re-adsorption by the iron oxides produced during the process (refer to the chemical equations in Figure 7.18).

8.3. Limitation of the research

Throughout performing the current research, the following limitations can be specified below:

1. Regarding sampling strategy, soil samples have been collected randomly, due to the difficulties in accessing all locations as the majority of them are private, and some land owners did not give permission for sampling. As a consequence, there will be some limitations of knowledge, for instance soil variability over a specific distance.

2. Sampling suspended sediment from the River Manifold would give a clear picture of the distribution of sediment- related heavy metals downstream, and consequent deposition in the floodplain samples.
3. Sampling twice in two summers can be useful as it can reflect the seasonal fluctuation of heavy metals concentration.
4. It would be more rational to construct background values for pollution assessment by selecting control locations, which are not affected by former human activities such as mining. This will give a better understanding of the actual situation of the pollution.

8.4. Implication of the research and suggestions for land uses

In this section the possible implications of the current research findings and recommendations for different land uses will be discussed in context of climate change.

Nowadays climate change is become an issue of great interest in many researches worldwide (Environment Agency, 2008), with human activities are considered to be the main factor which influences the composition of the Earth's atmosphere, and thereby, resulting in climate change, which in turns has a significant impact on the temperature and precipitation in many regions all over the world (Kay *et al*., 2006). For instance, according to Environment Agency (2008), in the last century the temperature of the Earth's surface has been raised by approximately 0.4 ^{o}C with an expected increase of about (1.4-5.8 ^{o}C) at the end of the current century. As a result, the major concern of that is the change in both the frequency and the magnitude of floods across the globe, this has been investigated by Knox (1993), who had made a model to predict and monitor the fluctuation in the magnitude and frequencies of the

Upper Mississippi valley. In addition, a research by Prudhomme et al. (2003) had been conducted to study the effect of climate change on the flood in the UK for the next 100 years using different models. These researchers highlighted that the rainfall will be increased and higher by 8% in 2050, and hence, the frequency of floods will be increased. Therefore, a significant increase in the rainfall and especially a seasonal precipitation will result in further flood events in the UK. However, in the warmer climate the ratio of evaporation will be increased, therefore the amount of the organic matter will be reduced, and it has been estimated that 16% of organic matter has been reduced in soils managed for grassland in England and Wales (DEFRA, 2006a). As a consequence the acidity of the soils will be increased with a possible change in heavy metal species and, thereby, increase the mobility and bioavailability of the metals (Kabata-Pendias, 2001). This will influence the result of the current study with regards to the bioavailability for which the organic matter content is indicated to be a significant factor. As a result, changing the soil organic matter content over a time should be taken a special consideration for a long-term bioavailable fraction assessment.

In the same way, climate change could change the soil pH, which is a crucial factor controlling the mobility and bioavailability of heavy metals, and it was found that in England and Wales the pH values has a reducing trend between the years 1982 and 1988 (Skinner et al., 1992). This might increase the bioavailable fraction of heavy metals to pastures, and hence, becoming more harmful to livestock grazing on the soils where pH has been changed. In addition, increasing the bioavailable fraction of metals may retard plant root growth and absorbing the necessary nutrients (Smith et al., 1996). In relation to the current study, the effect of pH was found to be a

significant factor in the speciation and leachability of heavy metals being studied; therefore, this factor should be paid a special attention when assessing the land for different uses.

To sum up, as a consequence of climate change, the changes of organic matter content and soil pH should be given a special consideration in the future, especially for long-term monitor of the heavy metals concentrations, bioavailability and the potential effects on the grazing livestock, pastures and using the land for different purposes. In addition, although in chapter 4 heavy metals levels have been assessed for different land uses, further contamination could be a concern for farmer and land owners in future due to climate change and further remobilisation of heavy metals associated sediments via additional frequent and severe floods. Therefore, a periodical heavy metal pollution assessment of the soil is very important to avoid pollutants accessing into the food chain and reduce the potential risk to human health and other organisms.

8.5. Suggestions for further work

Below is some suggested further research, which would help develop and provide further understanding of the heavy metal contamination at the study area (Ecton Hill):

1. Calculating the mass balance for the metals studied in this research by measuring the discharge of the River Manifold through several sections. This would help in identifying how much mass of these metals can be released and transferred from the Ecton Hill body. To this end, the results recorded from the leaching test in this study could be used to estimate the metal mass that might be washed out from mining heaps distributed over the study area.

2. The bioavailability of the metals studied, especially Cu, Pb, and Zn, was found to be elevated. As a result, these pollutants are most likely to be transferred to the human food chain when consuming products from grazing cattle and plant growing on the polluted soils. Therefore, it would be worth carrying out an analysis of the plants and stock products to reduce the potential harmful effects of the pollutants.
3. The floodplain soils in the study area are being used for agricultural purposes and stock rearing; therefore, it would be useful to investigate the seasonal effects of floods in regard to supplying stream sediment related heavy metals to the surrounding floodplain soils.
4. Anthropogenic inputs of heavy metals to the soils arise not only from mining activities, but also from other human activities, such as the application of fertilisers and animal manure in agriculture to enhance plant growing, which are well documented to provide significant quantities of pollutants to the soils. As a result, it would be worth monitoring the effects of these activities.
5. Due to the higher concentrations found for Cu, Pb, and Zn in the soil of the study area, using some soil reclamation techniques would be useful, for instance phytoremediation using plants that are efficient for removing pollutants from the soil and fixing nitrogen (nitrogen fixation) at the same time, and good examples for that are perennial lolium and clover trifolium.

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Appendices

Appendix A: Total heavy metals extracted using aqua regia microwave digestion of Ecton mining area topsoils.

Sample	Cu	Pb	Zn	Mn	Cr	Ni	V	Fe	Al
ES1	116	922	561	600.75	48.25	45.75	95.5	16771.75	15192.5
ES2	81.75	904.5	448.75	1388.25	44.25	27.25	92.25	22516	22346.75
ES3	68	239.25	293.75	1878.5	36.75	31.5	38.75	12563.75	15877.25
ES4	91.75	798.75	1010.5	2144.25	33	27.25	40.5	16102.25	19728
ES5	317.5	290.75	1424	2049.25	22	21	21.5	10425.5	8750.25
ES6	4501.5	2716.5	8126.25	1369.5	15	16.25	16.75	11109.25	4408.25
ES7	1124.5	36644.25	14378.25	456.75	12.25	16.5	13.25	6131.25	2707
ES8	143.5	1294.5	3853.5	292.25	13.75	14.75	15.5	2545	6657.25
ES9	2138	21165.75	10898.75	579	21.75	28.25	25.5	7624.75	10598.5
ES10	232	11028.25	1598.5	1145.5	9.75	11.25	13.25	4943.25	2356.75
ES11	154	1040	1359.25	1021.5	37.5	59.5	20.5	5810.75	10760.5
ES12	4774.75	585.75	3542	361	20	25.75	14.5	7428.25	2995
ES13	80.5	6976.75	10594.75	503.25	62.25	59.75	34.25	7760	14311.75
ES14	31	98.5	159.25	853.25	62	51.75	26.75	16818.75	10002.75
ES15	34.75	86.75	213	863	31.5	24.75	61.5	8711.75	11212.75
ES16	26.5	82.75	119.5	1174.75	28	23	40.75	12427.5	16256.25
ES17	11.75	39	68	930.25	73.5	50.25	35.25	9356.25	9104.25
ES18	32.75	245.75	515.75	877.25	33.25	56.5	16.5	13260.5	9943.5
ES19	35.25	440.25	450.25	658	19.25	28	28.5	4534.5	8300.75
ES20	42.25	100.5	193.75	1555.5	33	19.75	26.5	10221.75	14464.5
ES21	528.75	158	660.5	292.5	35.5	22	56	25222	22343
ES22	52.75	779.75	381.75	241	56.75	34.5	114	24029	22010.25
ES23	34	218	304.75	520.75	23.5	54.25	57	26812	14189.25
ES24	40.75	44	226.25	330	99	134.75	73.25	28851	22595
ES25	39	169.25	310.5	2008.5	62.25	46	57.75	13810.5	21776.5
ES26	363	5467.5	9003.75	320	16.5	76.25	25	11163.75	11683.25
ES27	94.25	259	665.75	1912	61.25	60.25	78.25	20882.75	34227.25
ES28	107.75	208	731	1376.25	59	80.75	16	9583.5	8954
ES29	86.25	342.75	306.5	1096.25	32.25	28.25	45.25	10254.25	16146.25
ES30	36	345.75	145.25	260.5	19.5	36.25	43.75	6879.75	10232.5
ES31	12.25	116.25	90.75	390	63.75	34.5	51.25	10345	12714.75
ES32	166.75	28.75	2471.5	127.5	1	14	0.5	206.75	162
ES33	551.25	547.5	1005	2029.5	23.25	23	23.75	12641.5	9945.5
ES34	33.25	986.25	162.25	710.25	28.75	13.75	14	6428.5	4880.75
ES35	353.25	16223.25	2661	3478.75	29.75	35.25	55	8021.25	10282
ES36	310.5	1028.75	1670.5	3220.25	29.5	42	31.75	18824.75	15878.25
ES37	5126	4923.75	5037.5	740.75	27.75	43.5	34.5	15077.75	12045.5

Appendix B: Total heavy metals extracted using aqua regia microwave digestion of Ecton mining area floodplain samples.

Sample	Cu	Pb	Zn	Mn	Cr	Ni	V	Fe	Al
MF1	31.5	48	131.5	399.75	31.75	21	21	13783.75	12358.75
MF2	112.25	164.25	306.75	594.25	30.25	26.75	34.5	17868.5	13041.25
MF3	309.75	152	207.25	454.25	33.5	22	13.25	12574	3381
MF4	94.5	216.25	293	1045.25	148.75	96.75	30.75	20706.75	15028.25
MF5	101.75	197.5	299.75	930.5	62.25	40.5	41	20186.5	17545.5
MF6	88.5	159.75	251.5	1082.75	30	25	34.5	16391	15724.5
MF7	103.5	186	328.5	1463.75	32.75	29.75	47.25	23665.25	17784.25
MF8	100.25	548.5	335.25	1634	36.25	40.25	39.5	23328.75	17166
MF9	82.25	152.25	275	1217.75	43	34.5	35.25	19866.25	15666.75
MF10	96.25	164	336	1263.75	36.25	29.75	41.25	19967.5	18790.25
MF11	353.5	490	1606.5	1509.75	24.25	35.75	40	20824.5	16509.75

Appendix C: XRF analysis of heavy metals of Ecton mining area topsoil samples

Sample	Cu	Pb	Zn	Mn	Cr	Ni	V
ES1	382	2660	1330	1320	168.7	109.3	231.5
ES2	154.6	642.7	503.9	723.8	113.9	24.8	101.1
ES3	108.1	373.4	484.8	2290	64.5	32.4	
ES4	164.9	1130	1370	2150	35.8	19.4	60.7
ES5	813.8	839.7	3530	5270	69.1	19.9	42.8
ES6	12610	12520	41250	4260			
ES7	2110	72030	73240	1170			
ES8	1040	8480	21850	1480	33.5	38.2	
ES9	5480	27760	50370	1660		0	
ES10	790.8	71960	9980	6890			
ES11	513.4	3340	4640	3130		123.4	
ES12	5870	3420	13370	1170		31.6	
ES13	251.4	8040	38710	1440	176.3	10	114.9
ES14	100.3	169.4	262.4	1440	75.7	39	88
ES15	120.1	206.6	423.5	1760	59.9	33.3	128.1
ES16	92.2	78	164.3	1010	71	21.4	89.8
ES17	68.7	61.9	109.8	1460	67.1	25.2	101.8
ES18	139.3	535.8	863	1490	169.8	80.5	105.8
ES19	192	2020	2260	3130	37.8	99	
ES20	108	156.8	365.5	2420	66.9	22.8	54.1
ES21	1080	334.9	885.1	450.8	87.6	35	110.3
ES22	148.3	1180	491	207.8	84.9		181.9

ES23	135.2	727.8	624.9	1090	225.7	105	146.5
ES24	142.6	143.8	402.7	517.1	134	192.3	203.8
ES25	87.6	307.5	478	2970	103.8	51.5	
ES26	389.1	12070	16610	698.7		41.6	
ES27	215.7	624	1160	3050	150.5	82.7	137.5
ES28	344.1	633.4	1080	3410	129.5	103.2	91.4
ES29	116.4	577.2	465.6	1810	70.8	31.9	95
ES30	150.9	1080	346.6	793.7	113.2	95.7	176.6
ES31	38	108.8	113.7	252.8	71.2		100.4
ES32	13980	9920	31210	2570		17.8	
ES33	10850	18880	20970	2060		72.9	
ES34	1020	47910	8810	10240			
ES35	118.1	2900	580.1	1430	78.3	24.6	86.7
ES36	1520	1730	2750	6240	67.6	20.6	61.5
ES37	702.9	1840	3560	6480	114.9	46	

Appendix D: XRF analysis of heavy metals of Ecton mining area floodplain samples.

Sample	Cu	Pb	Zn	Mn	Cr	Ni	V
MF1	123.3	193.6	343.4	1470	118.3	32.1	96.4
MF2	1150	1460	4740	4210	235.2	74.2	141.3
MF3	264.7	428.9	763.4	3010	110	45.6	115
MF4	251.1	376	605.9	2210	78.8	28.8	99.8
MF5	265.7	371.5	588.1	2320	102.5	26.4	121
MF6	250.7	374.6	585.3	2380	107.6	31.7	120.6
MF7	245.6	432.5	642.4	2550	110		121.9
MF8	187.3	447.8	578.8	1960	95.5	18.1	97.3
MF9	256.4	513.5	661.9	2310	103		116.5
MF10	365.4	712.3	833.7	2340	216.1	45.1	128.7
MF11	348.5	525.8	696.1	1820	115.2	52.5	115.7

Appendix E: Bioavailable fraction (EDTA extraction) of the selected heavy metals (mg/kg) in the collected soil samples at Ecton mining area.

sample	Cu	Pb	Zn	Mn	Cr	Ni	V
ES1	10.81	75.97	27.32	48.02	0.07	1.9	0.37
ES2	3.85	39.18	5.15	46.32	0.05	0.48	0.07
ES3	2.72	19.23	7.85	150.68	0.14	1.17	0.03
ES4	3.96	48.39	32.91	106.06	0.11	0.47	0.14
ES5	15.92	21.66	49.92	151.32	0.14	0.81	0.09
ES6	188.86	164.88	387.59	53.81	0.07	0.41	0.17
ES7	40.08	2244.4	433.68	21.07	0.07	0.25	0.44
ES8	20.38	233.55	172.18	18.97	0.04	0.86	0.12
ES9	101.67	993.58	528.36	18.06	0.06	0.7	0.4
ES10	6.22	1391.25	96.87	55.28	0.09	0.32	0.66
ES11	5.23	81.7	59.64	34.61	0.06	0.46	0.15
ES12	48.12	33.35	121.36	7.86	0.03	0.37	0.07
ES13	3.39	207.17	634.07	11.93	0.05	0.4	0.28
ES14	1.66	5.36	2.08	72.26	0.07	0.87	0.03
ES15	3.09	8.26	6.49	92.37	0.09	1.37	0.18
ES16	1.5	3.06	0.93	77.97	0.09	0.61	0.03
ES17	0.82	2.51	0.82	97.81	0.1	0.64	0.07
ES18	2.64	15.75	13.93	53.9	0.06	1.13	0.04
ES19	1.02	22.08	15.25	12.73	0.03	0.24	0.1
ES20	2.85	8.39	3.03	167.69	0.16	0.81	0.04
ES21	33.35	8.72	15.01	17.24	0.03	0.41	0.07
ES22	3.16	33.39	5.39	7.56	0.03	0.39	0.28
ES23	2.62	12.86	11.55	36.57	0.06	2.15	0.42
ES24	2.35	1.58	2.98	14.73	0.03	1.81	0.04
ES25	2.64	11.24	11.07	167.47	0.16	1.4	0.25
ES26	7.08	464.53	341.42	8.89	0.04	0.7	0.14
ES27	3.83	18.23	13.01	136.11	0.13	2.13	0.16
ES28	5.25	13.55	11.91	43.87	0.05	0.46	0.04
ES29	4.37	30.4	11.43	93.18	0.1	1.51	0.13
ES30	1	18.07	2.9	4.29	0.02	0.22	0.08
ES31	0.81	8	1.66	12.54	0.03	0.14	0.05
ES32	124.4	117.88	397.83	17.55	0.04	0.81	0.19
ES33	35.38	47.58	36.51	170.3	0.16	0.92	0.12
ES34	3.27	179.43	4.97	87.52	0.09	0.22	0.15
ES35	6.49	728.2	81.17	112.79	0.14	0.4	0.94
ES36	17.38	68.34	54.04	238.88	0.22	1.6	0.04
ES37	119.93	298.74	246.01	34.91	0.06	0.95	0.24

Appendix F: Bioavailable fraction (EDTA extraction) of the selected heavy metals (mg/kg) in the collected floodplain samples at Ecton mining area.

sample	Cu	Pb	Zn	Mn	Cr	Ni	V
MF1	2.37	4.3	6.22	35.9	0.05	0.66	0.01
MF2	8.43	12.53	8.36	54.54	0.06	0.79	0.03
MF3	8.69	17.72	10.23	67.05	0.07	0.84	0.04
MF4	6.47	11.27	8.31	67.84	0.08	0.71	0.02
MF5	6.9	13.03	8.51	75.49	0.08	0.68	0.04
MF6	6.86	12.64	8.44	100.8	0.1	0.81	0.05
MF7	7.25	10.97	9.65	92.2	0.09	1.03	0.04
MF8	7.2	10.81	9.42	101.59	0.1	1.11	0.03
MF9	6.69	9.89	9.12	75.89	0.08	0.82	0.03
MF10	7.83	15.11	17.1	95.31	0.1	0.89	0.07
MF11	23.45	31.8	80.79	117.55	0.13	1.07	0.22

Appendix G1: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continues next page)

Sample	Cu				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	16.8	11.2	15.2	128	62.8
ES2	1.2	9.6	14.4	59.2	51.6
ES3	0.8	2.4	5.2	144.8	57.2
ES4	1.2	2	1.2	84	25.2
ES5	1.6	10	5.2	312.8	311.2
ES6	17.6	120.8	150.4	4807.2	1097.2
ES7	5.2	326.8	169.2	454.4	448
ES8	4	44	27.2	579.2	150.8
ES9	3.6	1156.4	1096.8	1632.8	328.8
ES10	2.8	2.4	0.8	220.8	102.4
ES11	2	11.2	4.4	126.4	177.2
ES12	8	119.6	162.8	2669.6	2164
ES13	1.2	9.2	1.6	79.2	67.2
ES14	1.6	2.8	2	61.6	50
ES15	1.6	2	2.8	46.4	34.4
ES16	1.6	7.2	7.2	18.4	31.2
ES17	0.8	2	2	16	14.8
ES18	2	2	1.6	78.4	52.4
ES19	1.2	0.4	0	44	34
ES20	1.2	3.6	5.2	64.8	48.8
ES21	7.6	240.4	241.2	528.8	163.2
ES22	1.2	4.8	7.2	90.4	22.4
ES23	1.2	10.4	1.2	92.8	24.8
ES24	1.2	1.6	2.4	56	39.6
ES25	1.6	0.4	0	53.6	40.4
ES26	2	27.6	1.6	221.6	112
ES27	2.4	1.2	0	93.6	64
ES28	3.2	0.8	0	184.8	90
ES29	1.6	2.8	3.6	104.8	57.6
ES30	2	0.4	0	44.8	31.2
ES31	0.8	1.2	1.6	54.4	8.4
ES32	10.4	1329.2	848	7040	4395.2
ES33	15.6	24.4	8.8	983.2	350
ES34	2	5.2	7.2	84	43.2
ES35	3.2	2	0.4	327.2	179.2
ES36	3.2	32.4	48.8	439.2	245.6
ES37	24.4	46	10.4	6149.6	801.2

Appendix G2: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Pb				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	69.2	46	300.4	645.6	601.2
ES2	28	55.6	331.6	580.8	432
ES3	6.4	4.8	66	894.4	318.4
ES4	4.4	28	165.6	632	309.6
ES5	4.8	2.4	16.4	410.4	211.6
ES6	44.4	72.4	99.2	2865.6	1326.4
ES7	456	8951.2	7967.6	45592	22102.8
ES8	1308	532.8	434.4	3601.6	1379.2
ES9	394	4054.8	3842.8	7161.6	11246.8
ES10	1264.4	2100.8	1393.2	20907.2	6040.4
ES11	8	173.2	269.2	977.6	581.2
ES12	10.4	88.8	24	675.2	1320.8
ES13	136.8	1186.8	393.2	4238.4	2286.8
ES14	3.2	3.6	34	215.2	78.8
ES15	6.8	2	23.2	165.6	48
ES16	7.2	5.6	27.6	64.8	26.4
ES17	3.6	7.6	12.8	59.2	23.2
ES18	2.8	22	43.2	393.6	109.2
ES19	3.2	13.6	6	620	1709.6
ES20	2.4	2.8	36.4	191.2	82.4
ES21	7.6	11.2	50.4	146.4	130
ES22	65.6	31.2	121.2	601.6	431.6
ES23	2.4	12.8	18.8	232	294.8
ES24	1.2	2.8	2	58.4	43.6
ES25	2.4	1.2	3.2	247.2	162.4
ES26	610	3708.4	1157.2	7141.6	6354.8
ES27	2.4	3.6	7.2	401.6	109.2
ES28	3.2	5.6	2.8	406.4	128
ES29	3.6	11.6	97.2	741.6	138.4
ES30	3.6	10.4	3.6	563.2	237.2
ES31	5.6	33.6	31.6	176.8	59.6
ES32	62.4	686.8	339.6	2564.8	2911.2
ES33	4	10.4	30.4	1092	291.2
ES34	213.2	262	1432.4	1896.8	411.2
ES35	406	342.4	295.6	17167.2	5182
ES36	25.2	48.4	364.4	1838.4	432.8
ES37	241.6	128.8	59.6	4841.6	1430.4

Appendix G3: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Zn				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	138.4	121.6	96	134.4	344
ES2	22.4	33.2	22.8	68	384.8
ES3	11.2	44.8	88.8	673.6	358.4
ES4	15.6	333.6	287.6	615.2	320
ES5	11.6	287.2	436.8	608	1464.4
ES6	388.4	3061.2	3805.2	8747.2	2998
ES7	185.6	6988.4	7687.2	21674.4	20456
ES8	158.8	1665.2	2200	7194.4	3378
ES9	209.6	8720.8	5528.8	6633.6	3574
ES10	242	906.8	527.6	922.4	533.6
ES11	19.6	891.2	655.2	648	748.8
ES12	86.8	1108.4	548.8	2504.8	3932.4
ES13	175.2	10825.6	2640.4	8259.2	8449.2
ES14	10	26.8	27.6	90.4	236.4
ES15	9.6	40.4	74	95.2	258.4
ES16	8	7.6	8.8	53.6	105.2
ES17	3.2	10.4	8	36	68.8
ES18	34.8	147.6	103.6	274.4	245.6
ES19	10.4	84.8	65.2	466.4	330.4
ES20	5.2	25.2	30.8	88.8	270.8
ES21	33.6	178.4	94.8	196	278
ES22	44	22.4	14.4	97.6	247.6
ES23	13.2	122.4	92.8	212	154
ES24	3.6	16.8	14	77.6	214
ES25	4	54	64	196	252
ES26	224	4232.8	755.2	6904	13148.8
ES27	4.8	49.2	104	282.4	465.2
ES28	6.8	62.8	38.8	415.2	443.6
ES29	14.8	87.6	97.6	195.2	256.8
ES30	0.8	18.4	4.8	115.2	145.6
ES31	3.6	13.2	3.2	163.2	65.2
ES32	131.6	6394.8	1688.4	7444	9973.6
ES33	19.6	233.2	249.2	548	968.4
ES34	17.6	46	36.8	178.4	311.6
ES35	148	433.2	434.8	1942.4	874.4
ES36	271.2	317.2	369.6	1160.8	1490.8
ES37	748.8	1072.8	1054.8	3714.4	1256.4

Appendix G4: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Mn				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	49.2	73.2	871.2	89.6	154
ES2	24.8	45.6	1157.2	191.2	658
ES3	26.4	96	3855.2	443.2	324.8
ES4	12.4	203.6	2581.2	328.8	178.4
ES5	2.4	78.4	3148.4	520	450.8
ES6	25.2	92.8	1964	600	192.8
ES7	1.6	49.6	640.4	124.8	273.2
ES8	7.6	67.6	528	287.2	456.4
ES9	1.2	59.2	382.8	75.2	335.2
ES10	9.6	924	1190.8	356	518.4
ES11	4.4	160	1014	351.2	798.8
ES12	3.6	76.4	224	495.2	88.8
ES13	3.2	115.6	533.2	233.6	156.4
ES14	114	218.8	1852	351.2	386.8
ES15	50.8	115.2	1504.8	179.2	111.2
ES16	82	75.6	1792	262.4	190.8
ES17	65.2	93.6	1618	208.8	162.8
ES18	30.4	138.4	946.8	236	238.8
ES19	11.6	112.8	571.6	402.4	239.6
ES20	64.4	181.2	3377.2	500	313.2
ES21	18.4	48.4	205.6	41.6	140.4
ES22	18.4	20.8	101.6	36.8	195.2
ES23	34.4	111.6	398.4	108	172.8
ES24	17.6	36.8	195.6	60.8	232.4
ES25	10	169.2	2656.8	1039.2	286.4
ES26	0.8	73.2	108.4	208.8	153.6
ES27	12.4	150.4	1758	628.8	149.6
ES28	24.4	374	1319.6	1048.8	236
ES29	28	125.6	1868.4	334.4	149.2
ES30	6.4	58.8	187.6	142.4	53.6
ES31	10	20	184.8	71.2	118.4
ES32	2	262.4	403.2	675.2	357.2
ES33	50	243.2	2797.2	765.6	319.2
ES34	72	104.4	1996	429.6	305.2
ES35	29.6	150	2297.2	1640	587.2
ES36	165.6	204	5866.8	1075.2	436.4
ES37	97.2	93.6	486.4	323.2	95.6

Appendix G5: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Cr				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	12	0	0.4	8.8	14
ES2	0	0	0.4	11.2	14
ES3	0	0	0	8	15.2
ES4	0	0	0	6.4	8.4
ES5	0	0	8.4	4	10
ES6	0	0	0	4.8	10.4
ES7	0	0.4	0	3.2	10
ES8	0	0	0	2.4	25.2
ES9	0	0.4	0	2.4	12
ES10	0	0	0	6.4	8.8
ES11	0	0	0	4	24.8
ES12	0	0	0	4	5.6
ES13	0	0.4	0	4.8	7.2
ES14	0	0	0	11.2	14
ES15	0	0	0	10.4	12.4
ES16	0	0	0	11.2	10.4
ES17	0	0	0	11.2	10.8
ES18	0	0	0	9.6	12
ES19	0	0	0	6.4	8
ES20	0	0	0.4	14.4	16
ES21	0	0	0	12	12.8
ES22	0	0	0.4	27.2	12
ES23	0	0	0	17.6	10.4
ES24	0	0	0	14.4	12.4
ES25	0	0	0	11.2	14.8
ES26	0	0	0	2.4	14.4
ES27	0	0	0	11.2	10.4
ES28	0	0	0	5.6	5.6
ES29	0	0	0.4	13.6	12.4
ES30	0	0	0	8.8	6
ES31	0	0	0.4	12	6
ES32	0	0.4	0	3.2	4.4
ES33	0	0	0	8	9.6
ES34	0	0	0.4	16	12.8
ES35	0	0	0	13.6	18.8
ES36	0	0	0.4	16	14.8
ES37	0	0	0	9.6	8.4

Appendix G6: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Ni				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	16.4	8.4	9.2	8	35.6
ES2	1.2	2.4	3.2	3.2	18.8
ES3	0.8	3.2	17.6	8.8	23.2
ES4	0.4	2	4.4	8.8	12
ES5	0	0.8	7.6	12.8	20
ES6	0	2	2.4	9.6	11.6
ES7	0	2.8	3.6	8.8	19.6
ES8	0.8	8.8	7.2	38.4	16
ES9	0	7.6	6.8	21.6	8
ES10	0.4	2	1.2	11.2	12.8
ES11	0	6	15.6	28	57.6
ES12	0	3.2	2.8	20	14.8
ES13	0	4.8	3.2	40	33.2
ES14	2.8	5.2	10.8	13.6	36
ES15	0.8	3.6	12.8	10.4	20.8
ES16	2.4	1.6	6	4.8	25.6
ES17	1.2	2.4	6.4	5.6	13.2
ES18	0.8	5.2	8	19.2	37.6
ES19	0	0.8	0.8	25.6	23.6
ES20	0.4	2.8	9.6	8	18
ES21	0.8	2.8	2.8	8	17.6
ES22	2	1.6	1.2	4.8	7.6
ES23	2.4	12	17.6	35.2	28
ES24	4	11.2	10.8	30.4	77.6
ES25	0	2	2.4	38.4	29.2
ES26	0	8.4	2.8	35.2	13.2
ES27	0	1.6	6	47.2	30.4
ES28	0	2	1.2	52.8	39.2
ES29	0.4	4.4	12	13.6	21.2
ES30	0	0.8	0.4	17.6	47.6
ES31	0.4	0.8	0.4	3.2	5.2
ES32	-0.4	10.8	9.2	42.4	16.4
ES33	0	1.6	5.2	17.6	18
ES34	0.4	1.2	1.2	5.6	12.4
ES35	0	0.8	0.4	19.2	19.6
ES36	4.4	5.2	20.8	14.4	32.4
ES37	1.2	2.4	1.6	26.4	20.8

Appendix G7: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	V				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	13.2	0.4	8.4	39.2	50.4
ES2	0.4	0	4	25.6	56.4
ES3	0.4	0	1.6	13.6	25.2
ES4	0	0.4	1.2	12	13.6
ES5	0	0.4	0.8	5.6	18.8
ES6	0.4	0.4	0.8	8.8	16.8
ES7	0	0.4	2	5.6	18.8
ES8	0	0.4	0.8	3.2	32.8
ES9	0	0.4	2.8	1.6	15.6
ES10	0.4	0.4	0.8	10.4	17.6
ES11	0	0.4	1.6	4.8	22.8
ES12	0.4	0.4	1.6	5.6	12
ES13	0	0.4	2.4	12	13.2
ES14	0	0.4	0.8	15.2	30.8
ES15	0.4	0	3.6	32.8	44.4
ES16	0.4	0	2.4	16	20.8
ES17	0	0	4	24	27.2
ES18	0.4	0.4	0.4	13.6	14.4
ES19	0.4	0.4	0.8	16	17.2
ES20	0.4	0	1.6	13.6	23.6
ES21	0.4	0.4	2.4	10.4	28
ES22	0	0.4	8	53.6	47.6
ES23	0.4	0	4	33.6	34.4
ES24	0	0	1.2	16.8	44.8
ES25	0.4	0.4	0.8	20	26.8
ES26	0	0.4	1.2	1.6	21.6
ES27	0.4	0.4	0.4	18.4	17.6
ES28	0.4	0	0.4	6.4	8.4
ES29	0	0	1.6	25.6	27.6
ES30	0.4	0.8	0.8	21.6	20
ES31	0.4	0	3.6	17.6	21.2
ES32	0	0.4	3.2	4	14
ES33	0.4	0.4	0.8	7.2	18
ES34	0	0.4	2.8	22.4	23.2
ES35	0.4	0.4	0.8	30.4	36.4
ES36	0	0	1.2	16	26.8
ES37	0.4	0.4	0.4	12.8	16.8

Appendix G8: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Fe				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	13.2	20.8	3389.6	3568	25121.2
ES2	1.6	9.2	2090.8	2976.8	32368
ES3	1.2	4.8	1159.2	1619.2	19042
ES4	1.2	8	962.4	2457.6	12869.2
ES5	0.8	3.2	258.8	225.6	18312.4
ES6	3.6	8	313.6	1112.8	16805.2
ES7	0.8	8.8	267.6	162.4	15306.8
ES8	0	12.8	213.2	609.6	8308.4
ES9	0.4	10	595.2	334.4	6590.8
ES10	13.6	7.2	119.2	704	8299.6
ES11	0.4	5.6	332.8	380	10159.6
ES12	2	10	106	426.4	12213.2
ES13	0.4	3.6	98	432.8	14481.6
ES14	2.8	12.8	1618.8	5838.4	35360.4
ES15	1.2	4.4	731.2	1681.6	14368.4
ES16	2.8	8.4	1261.2	2209.6	15072
ES17	2.4	6	989.2	2060.8	13272
ES18	0.8	10.8	877.6	3688.8	18515.2
ES19	3.2	5.6	20	1065.6	6218.8
ES20	3.2	8	1409.2	3169.6	20858
ES21	0.8	19.6	2871.2	2483.2	33163.2
ES22	4.4	22.8	2856	5621.6	22656
ES23	4.4	29.6	3026	9402.4	32950
ES24	2.4	14.4	1551.6	6744	40811.2
ES25	2	6.4	206	3090.4	22219.6
ES26	0.4	21.6	344	1312	11411.6
ES27	2	9.2	468.4	5192	20475.2
ES28	1.6	3.2	10	1252.8	12694.4
ES29	2	5.6	870	3575.2	14737.6
ES30	2	11.2	5.2	856	9525.6
ES31	3.2	12.4	1156	2640.8	7912.8
ES32	2	19.6	554.8	840.8	18241.2
ES33	3.2	9.2	370	1204	18314.8
ES34	2	8	1222.8	3156	16669.6
ES35	6	9.2	125.2	3352	13521.6
ES36	3.6	6.8	2092.8	3316.8	26855.2
ES37	6.8	18.4	199.6	4292	16034

Appendix G9: Five steps sequential extraction results (mg/kg) for topsoil samples collected form Ecton mining area (continued).

Sample	Al				
	Exchangeable	Carbonate	Fe/Mn	Organic	Residual
ES1	18	144	324.8	1030.4	5718.8
ES2	3.2	272.4	534.4	1495.2	8498
ES3	2	154.4	578.4	2480.8	9195.6
ES4	1.6	44.4	226	2055.2	6180
ES5	1.6	14.8	10.8	521.6	5480.4
ES6	4.4	15.6	8.8	626.4	3453.2
ES7	2	130	58.8	169.6	2524.4
ES8	1.6	22	14.4	131.2	14266.8
ES9	2.4	160.8	135.2	140	6081.6
ES10	1.04	20.4	11.6	516.8	3862.4
ES11	1.6	56.4	31.2	202.4	11682
ES12	3.6	31.2	10.8	300	1991.6
ES13	2.4	61.6	19.6	387.2	2819.6
ES14	4.4	154	503.6	1841.6	7227.2
ES15	2.8	48.4	637.2	1940	4864.4
ES16	43.2	396.8	674	1659.2	5832.8
ES17	3.2	299.6	641.6	1952.8	6099.6
ES18	3.6	102	379.6	2303.2	8157.6
ES19	6.4	16.8	8.4	357.6	2841.2
ES20	4	211.2	673.6	2252.8	10388.8
ES21	2.4	114.8	300.8	1233.6	7772
ES22	5.6	230.8	527.2	1726.4	8676.8
ES23	2.8	88.8	319.2	1546.4	6178.8
ES24	3.6	154	390	2064	8515.6
ES25	4.4	19.6	12.4	1668	6567.2
ES26	3.2	106.8	35.2	71.2	10218
ES27	4.4	16	37.2	1892	5174
ES28	4	11.6	9.2	368.8	3491.2
ES29	4	106.8	487.2	2333.6	6673.6
ES30	4.4	38.4	8.4	472	3208
ES31	4	327.2	446.4	1067.2	4378
ES32	3.6	93.2	33.6	236	1086.4
ES33	4.4	19.6	8.8	567.2	4688.4
ES34	3.6	249.2	577.6	2029.6	9336
ES35	6.8	16	9.6	864.8	8494
ES36	5.2	174.4	419.6	2345.6	8486
ES37	13.6	38	18.4	1138.4	2631.2

Appendix H: Leaching test results (amount leachable mg/kg) for topsoil samples collected form Ecton mining area.

samples	Cu	Pb	Zn	Mn	Cr	Ni	V
ES1	9	48.5	48.5	9.5	0.3	1.5	1.7
ES2	6.2	34.2	24.7	21.7	0.6	0.9	1.6
ES3	0.2	1.1	5.2	5.5	0.1	0.2	0.1
ES4	2.1	15.3	30	13.2	0.1	0.3	0.1
ES5	3.1	2.6	15.2	5.3	0.1	0.1	0
ES6	28.8	9.9	52.7	1.7	0.1	0.1	0
ES7	2.7	92	63.8	0.5	0.1	0	0
ES8	5	159.7	380.1	6.2	1.5	2.8	1.8
ES9	70	199.9	742.4	3.8	0.6	0.5	0.6
ES10	1.2	118	22.4	5.5	0	0.1	0.1
ES11	0.7	10.3	35.8	3.3	0.1	0.3	0
ES12	22.2	27.7	55.2	1.8	3	0.5	0.7
ES13	3.9	209.9	1937.7	10.6	0.4	2	0.7
ES14	0.4	3.3	0.8	11.6	0.1	0.3	0.1
ES15	0.7	2.7	9.8	11	0.1	0.3	0.4
ES16	1.1	4.4	10.8	25	0.6	0.8	0.6
ES17	0.3	0.1	3.7	5.5	0.1	0.2	0.1
ES18	1.9	6.6	248.4	7.9	0.2	0.8	0.4
ES19	0.4	2.9	4.5	2.4	0.2	0.2	0.1
ES20	0.3	0.8	3.5	10.4	0.1	0.2	0.1
ES21	28.7	9.1	29.8	3.2	0.1	0.5	0.5
ES22	0.2	3.1	5	0.8	0.1	0.1	0.1
ES23	0.3	4.2	5.4	2.8	0.1	0.5	0.2
ES24	0.1	0	1.9	0.6	0.1	0.6	0
ES25	3.9	2.4	4	10.4	0.1	0.2	0.1
ES26	8.1	124.5	303.1	0.7	0.1	0.7	0.1
ES27	1.6	4.6	56.3	13.6	0.1	0.6	0.4
ES28	13	6.2	27.3	15.1	0.6	0.7	0.1
ES29	1.9	50.1	30.4	6	0	0.5	0.3
ES30	0.2	14.7	3.2	4.6	0.1	0.3	0.2
ES31	0.7	2.3	6.3	3.2	0	0.1	0.2
ES32	3.6	3.2	29.5	0.5	0.1	0	0
ES33	8.9	7.2	55.5	12.4	0.1	0.2	0.2
ES34	1.1	21.7	43.8	5	0	0.1	0.1
ES35	2.8	106.5	39.8	8	0	0.3	0.1
ES36	4.6	7.2	97.2	15.3	0.1	0.5	0.1
ES37	24	18.5	63.4	1.6	0.1	0.2	0.1

Appendix I: Leaching test results (% amount leachable) for topsoil samples collected form Ecton mining area.

samples	Cu	Pb	Zn	Mn	Cr	Ni	V
ES1	7.76	5.26	8.65	1.58	0.62	3.28	1.78
ES2	7.58	3.78	5.50	1.56	1.36	3.30	1.73
ES3	0.29	0.46	1.77	0.29	0.27	0.63	0.26
ES4	2.29	1.92	2.97	0.62	0.30	1.10	0.25
ES5	0.98	0.89	1.07	0.26	0.45	0.48	0.00
ES6	0.64	0.36	0.65	0.12	0.67	0.62	0.00
ES7	0.24	0.25	0.44	0.11	0.82	0.00	0.00
ES8	3.48	12.34	9.86	2.12	10.91	18.98	11.61
ES9	3.27	0.94	6.81	0.66	2.76	1.77	2.35
ES10	0.52	1.07	1.40	0.48	0.00	0.89	0.75
ES11	0.45	0.99	2.63	0.32	0.27	0.50	0.00
ES12	0.46	4.73	1.56	0.50	15.00	1.94	4.83
ES13	4.84	3.01	18.29	2.11	0.64	3.35	2.04
ES14	1.29	3.35	0.50	1.36	0.16	0.58	0.37
ES15	2.01	3.11	4.60	1.27	0.32	1.21	0.65
ES16	4.15	5.32	9.04	2.13	2.14	3.48	1.47
ES17	2.55	0.26	5.44	0.59	0.14	0.40	0.28
ES18	5.80	2.69	48.16	0.90	0.60	1.42	2.42
ES19	1.13	0.66	1.00	0.36	1.04	0.71	0.35
ES20	0.71	0.80	1.81	0.67	0.30	1.01	0.38
ES21	5.43	5.76	4.51	1.09	0.28	2.27	0.89
ES22	0.38	0.40	1.31	0.33	0.18	0.29	0.09
ES23	0.88	1.93	1.77	0.54	0.43	0.92	0.35
ES24	0.25	0.00	0.84	0.18	0.10	0.45	0.00
ES25	10.00	1.42	1.29	0.52	0.16	0.43	0.17
ES26	2.23	2.28	3.37	0.22	0.61	0.92	0.40
ES27	1.70	1.78	8.46	0.71	0.16	1.00	0.51
ES28	12.06	2.98	3.73	1.10	1.02	0.87	0.63
ES29	2.20	14.62	9.92	0.55	0.00	1.77	0.66
ES30	0.56	4.25	2.20	1.77	0.51	0.83	0.46
ES31	5.71	1.98	6.94	0.82	0.00	0.29	0.39
ES32	2.16	11.13	1.19	0.39	10.00	0.00	0.00
ES33	1.61	1.32	5.52	0.61	0.43	0.87	0.84
ES34	3.31	2.20	27.00	0.70	0.00	0.73	0.71
ES35	0.79	0.66	1.50	0.23	0.00	0.85	0.18
ES36	1.48	0.70	5.82	0.48	0.34	1.19	0.31
ES37	0.47	0.38	1.26	0.22	0.36	0.46	0.29

Appendix J1: Cation Exchange Capacity (CEC) results (meq/100g soil) for topsoil samples at the study area

Samples	Ca^{2+} (meq/100g)	Mg^{2+}(meq/100g)	Na^{1+}(meq/100g)	K^{1+}(meq/100g)	CEC (meq/100g)
ES1	426.4	50.8	70.6	10.1	557.96
ES2	216.4	44.9	42.1	13.8	317.22
ES3	451.2	38.7	128.7	3.4	621.96
ES4	482.2	83.9	27.8	14.8	608.79
ES5	402.6	52.8	60.5	11.5	527.37
ES6	612.4	67.9	21.6	11.0	712.88
ES7	222.2	63.9	61.9	3.4	351.42
ES8	315.2	35.1	4.9	27.1	382.26
ES9	204.4	7.9	12.3	5.2	229.83
ES10	289.8	45.9	2.8	7.4	345.85
ES11	306	18.7	15.1	4.4	344.22
ES12	360.8	4.9	9.7	3.8	379.24
ES13	228.8	8.5	9.2	4.6	251.15
ES14	281	36.4	32.5	11.0	360.96
ES15	339.2	30.5	13.4	5.0	388.10
ES16	147.6	20.7	13.6	16.8	198.60
ES17	206.8	16.7	10.1	1.9	235.55
ES18	643.8	99.3	35.7	11.7	790.46
ES19	580.8	22.6	10.3	6.0	619.72
ES20	267.6	30.2	19.0	2.6	319.28
ES21	377.6	26.2	22.6	0.3	426.75
ES22	340.6	26.6	59.1	0.5	426.80
ES23	367.6	26.2	25.4	0.9	420.14
ES24	582.8	31.8	24.3	10.6	649.59
ES25	735.6	142.3	41.6	48.8	968.26
ES26	117.4	8.9	5.0	4.4	135.69
ES27	655.6	152.5	15.5	10.4	833.97
ES28	740.6	46.2	8.9	19.7	815.44
ES29	520.6	59.3	18.6	3.1	601.62
ES30	656.6	16.7	3.5	4.3	681.10
ES31	614.4	95.1	45.7	8.0	763.20
ES32	161.4	5.6	3.7	0.3	170.93
ES33	460.4	104.9	30.1	2.6	597.96
ES34	203	48.9	41.6	4.8	298.23
ES35	545.8	154.1	88.7	12.2	800.77
ES36	163	72.5	210.1	8.7	454.24
ES37	1162.4	76.1	26.8	7.2	1272.41

Appendix J2: Cation Exchange Capacity (CEC) results (meq/100g soil) for floodplain samples at the study area

Samples	Ca^{2+} (meq/100g)	Mg^{2+}(meq/100g)	Na^{1+}(meq/100g)	K^{1+}(meq/100g)	CEC (meq/100g)
MF1	243.6	33.1	225.0	8.8	510.56
MF2	373.6	27.5	46.4	0.6	448.19
MF3	418.8	20.3	39.7	0.0	478.78
MF4	242	23.0	38.1	1.2	304.27
MF5	306.8	30.5	48.3	2.1	387.79
MF6	338.4	36.1	39.7	2.4	416.47
MF7	265.6	24.9	31.8	1.1	323.47
MF8	292.4	34.8	51.5	5.1	383.75
MF9	321.6	40.0	35.3	2.8	399.67
MF10	455.4	51.1	29.0	29.1	564.64
MF11	927.4	60.0	21.4	35.3	1044.09

Appendix K1: PH, Eh, organic matter and TOC analysis for topsoil samples.

Sample	pH_value	Eh(mV)	Organic matter %	TOC (%)
ES1	5.72	-157	19.20	10.44
ES2	5.78	78	12.51	6.22
ES3	5.77	-138	10.20	5.11
ES4	6.75	-62	20.19	9.45
ES5	7.75	173	12.18	6.56
ES6	6.61	78	40.90	20.78
ES7	6.33	79	9.29	6.23
ES8	6.55	59	8.86	4.78
ES9	7.2	100	7.71	4.29
ES10	6.87	104	24.60	13.19
ES11	7.47	43	6.13	3.57
ES12	7.39	57	7.34	4.27
ES13	7.29	54	55.53	32.28
ES14	6.08	91	12.35	7.18
ES15	6.68	28	8.86	5.15
ES16	5.24	-152	10.62	6.17
ES17	5.61	-159	8.54	4.97
ES18	6.62	44	15.05	8.75
ES19	7.37	89	13.84	8.05

ES20	6.06	32	13.72	7.98
ES21	6.47	57	11.66	6.78
ES22	5.41	-91	17.32	10.07
ES23	6.4	-25	20.43	11.88
ES24	5.98	-40	16.35	9.51
ES25	7.29	61	17.07	9.93
ES26	6.98	218	6.55	3.81
ES27	7.15	-24	24.65	14.33
ES28	7.44	56	16.25	9.45
ES29	6.48	48	19.00	11.05
ES30	7.29	-43	14.02	8.15
ES31	5.6	98	10.45	6.07
ES32	7.12	68	4.52	2.63
ES33	7.09	54	15.20	8.84
ES34	5.7	-264	13.01	7.57
ES35	6.76	11	43.75	25.44
ES36	5.39	-98	12.74	7.41
ES37	6.43	106	42.94	24.96

Appendix K2: PH, Eh, organic matter and TOC analysis for floodplain samples.

Sample	pH_value	Eh(mV)	Organic_M%	TOC (%)
MF1	5.93	100	6.91	4.01
MF2	6.05	125	9.54	5.54
MF3	6.11	118	6.31	3.67
MF4	5.62	69	10.53	6.12
MF5	5.57	25	10.90	6.34
MF6	5.89	61	8.97	5.22
MF7	5.7	118	11.72	6.81
MF8	5.7	45	13.06	7.59
MF9	5.94	135	10.76	6.26
MF10	6.41	22	14.15	8.23
MF11	6.99	38	22.23	12.92

Appendix L: Showing the percentage content of the main three granulometric classes (clay, silt and sand) for the collected topsoil and floodplain samples.

Topsoil samples			
samples	**% Clay**	**% silt**	**% sand**
ES1	12.66	87.34	0.00
ES2	11.03	40.24	48.73
ES3	19.80	80.20	0.00
ES4	6.51	32.97	60.52
ES5	0.00	40.55	59.45
ES6	2.41	46.02	51.57
ES7	0.00	15.69	84.31
ES8	21.75	78.25	0.00
ES9	18.38	77.46	4.16
ES10	24.43	75.57	0.00
ES11	28.58	71.42	0.00
ES12	0.00	76.76	23.24
ES13	23.10	76.90	0.00
ES14	10.56	35.82	53.62
ES15	0.00	61.11	38.89
ES16	25.73	74.27	0.00
ES17	0.00	64.60	35.40
ES18	22.59	77.41	0.00
ES19	8.08	33.41	58.52
ES20	0.00	28.74	71.26
ES21	15.09	27.19	57.72
ES22	6.64	20.13	73.23
ES23	7.04	33.52	59.44
ES24	16.81	44.96	38.23
ES25	24.75	65.92	9.33
ES26	11.33	38.34	50.33
ES27	10.50	30.88	58.61
ES28	11.96	43.57	44.47
ES29	0.00	50.35	49.65
ES30	0.00	25.58	74.42
ES31	0.00	19.30	80.70
ES32	5.74	29.36	64.89
ES33	8.14	35.70	56.16
ES34	14.62	50.33	35.05
ES35	0.00	38.77	61.23
ES36	9.48	40.09	50.43
ES37	2.29	17.46	80.25
Floodplain samples			
samples	**% clay**	**% silt**	**% sand**
MF1	0.00	20.85	79.15
MF2	8.96	37.47	53.56
MF3	1.70	6.67	91.63
MF4	20.86	57.26	21.88
MF5	18.27	81.73	0.00
MF6	23.32	76.68	0.00
MF7	15.53	64.60	19.88
MF8	9.70	35.56	54.75
MF9	15.33	61.12	23.55
MF10	19.20	80.80	0.00
MF11	19.77	80.23	0.00

Appendix M1: Geographic coordinates of topsoil sample sites (British National Grid)

Sample	Easting	Northing
ES1	410308	358031
ES2	410394	357777
ES3	410334	357292
ES4	410091	357345
ES5	409799	358244
ES6	409924	358314
ES7	410080	358052
ES8	410250	357781
ES9	410255	357570
ES10	409974	357846
ES11	409875	357921
ES12	409600	358293
ES13	409540	358040
ES14	409068	357755
ES15	409397	357629
ES16	409152	357099
ES17	409233	356434
ES18	409834	356837
ES19	410061	357990
ES20	409804	358519
ES21	410505	358075
ES22	410585	357722
ES23	410506	356701
ES24	410645	357012
ES25	410339	357157
ES26	410222	358058
ES27	410017	358815
ES28	409397	358508
ES29	409543	357869
ES30	409390	357479
ES31	409740	357546
ES32	409740	358208
ES33	409776	358253
ES34	409898	357865
ES35	409869	357784
ES36	410003	358144
ES37	409634	358151

Appendix M2: Geographic coordinates of floodplain sample sites (British National Grid)

Sample	Easting	Northing
MF1	409175	357800
MF2	409177	357806
MF3	409181	357813
MF4	409186	357820
MF5	409182	357816
MF6	409188	357825
MF7	409189	357828
MF8	409191	357831
MF9	409193	357835
MF10	409195	357838
MF11	409197	357841

Appendix N: List of Publications

World Academy of Science, Engineering and Technology
International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering Vol:11, No:4, 2017

GIS-Based Spatial Distribution and Evaluation of Selected Heavy Metals Contamination in Topsoil around Ecton Mining Area, Derbyshire, UK

Zahid O. Alibrahim, Craig D. Williams, Clive L. Roberts

***Abstract*—**The study area (Ecton mining area) is located in the southern part of the Peak District in Derbyshire, England. It is bounded by the River Manifold from the west. This area has been mined for a long period. As a result, huge amounts of potentially toxic metals were released into the surrounding area and are most likely to be a significant source of heavy metal contamination to the local soil, water and vegetation. In order to appraise the potential heavy metal pollution in this area, 37 topsoil samples (5-20 cm depth) were collected and analysed for their total content of Cu, Pb, Zn, Mn, Cr, Ni and V using ICP (Inductively Coupled Plasma) optical emission spectroscopy. Multivariate Geospatial analyses using the GIS technique were utilised to draw geochemical maps of the metals of interest over the study area. A few hotspot points, areas of elevated concentrations of metals, were specified, which are presumed to be the results of anthropogenic activities. In addition, the soil's environmental quality was evaluated by calculating the Mullers' Geoaccumulation index (I geo), which suggests that the degree of contamination of the investigated heavy metals has the following trend: Pb > Zn > Cu > Mn > Ni = Cr = V. Furthermore, the potential ecological risk, using the enrichment factor (EF), was also specified. On the basis of the calculated amount or the EF, the levels of pollution for the studied metals in the study area have the following order: Pb>Zn>Cu>Cr>V>Ni>Mn.

***Keywords*—**Heavy metals, GIS, multivariate analysis, geoaccumulation index, enrichment factor.

I. Introduction

THERE are many anthropogenic causes of environmental pollution by heavy metals. However, different industrial operations and urban improvements are considered to be the significant drivers for environmental contamination [48], [55]. As a result, nowadays environmental pollution by potentially toxic metals and their consequences for human health and organisms on the whole have become a key concern for many researchers worldwide.

Since heavy metals, unlike organic compounds, are non-biodegradable, they seem to accumulate in human and living organisms and cause various diseases, for instance damage to the liver and nervous system, digestive disorders and kidney problems [19], [33]. Heavy metals can discharge into the environment via both natural and anthropogenic sources. Natural sources include the weathering and breaking down of parent rocks, while anthropogenic sources include various human activities such as industrial processes, mining waste, agricultural application of fertilizers and sewage [14], [47].

To deal with heavy metal contamination, some techniques are needed such as Geographic Information System (GIS). GIS is a computerised data system that has the ability to display, simulate and measure problems related to environmental components (i.e. soil, air and water) [34]. In addition, this technique enables researchers to identify the relationship between pollutants, e.g. rare earth elements, and environmental constituents such as soil by analysing multilayers of these pollutants with different type of soils [6]. According to [50], GIS-based maps are very important for studies related with environmental investigations due to their ability to visualize the relationship between different lands features and environmental datasets. Moreover, GIS is a powerful tool for soil contamination research [32]. For example, [59] used the spatial distribution of heavy metals using GIS to indicate areas of soil polluted with heavy metals (i.e. hotspots, areas of high heavy metal concentration surrounded by areas of relatively low concentration). Therefore the GIS technique can help the investigator gain more insight into the present pollution as it gives a map with different colours making it easy to distinguish between polluted and unpolluted areas. Furthermore, using the geostatistical methods for pollution assessment enables researchers to use different spatial interpolation techniques, with a special focus on kriging and its different forms [5]. In addition, [3] highlighted that spatial distribution and the display of contaminated metals in an area of interest are very important as they give a better understanding with respect to the source of the pollutants, the pathway of exposure and the expected risk. Therefore, the spatial distribution of potentially toxic metals via the GIS approach has been widely used in estuarine environments [26] to evaluate the ecotoxicological influences of trace elements on organisms in the area of interest. For reasons mentioned above, in the current study the inverse distance weighted (IDW) method of the GIS software was used to identify areas contaminated with heavy metals. Heavy metal pollution has become a problem of great concern worldwide. These chemical materials have been introduced

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Assessment of bioavailability of some potential toxic metals in mining-affected soils using EDTA extraction and principle component analysis (PCA) approach, Derbyshire, UK

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Abstract

The current study area has long mining history for copper, lead, and zinc. As a result, these metals may have elevated levels and pose a potential risk to the surrounding area. This area is currently being used for agriculture and sheep rearing, therefore, the bioavailable fraction of some selected heavy metals namely (Cu, Pb, Zn, Mn, Cr, Ni, and V) has been evaluated using 0.01 M EDTA procedure, as this would help for better understanding of the risk that these heavy metals can pose to living organisms. A total of 51 samples of topsoils, floodplain soils, and stream sediment soils were collected and analysed for their total concentrations using ICP (Inductively Coupled Plasma) optical emission spectroscopy. Results show that, depending on the bioavailable ratio, soil samples have the biggest EDTA extractable amount for all studied metals, except for Mn and Cr for which highest levels were found in the floodplain samples. However, based on national bioavailable mean amount in England and Wales, the amount of EDTA metal extractable for all selected metals from soil samples are exceeded the national average amounts of England and Wales, except for Mn and Ni, whereas in floodplain and stream sediment samples, all EDTA metals extractions are lower than the national mean levels, except Cu and Zn for flood plan samples. Principal component analysis (PCA) technique was performed to investigate how the bioavailable fractions of studied metals and factors namely (organic matter contents, soil pH, and different granulometric ranges) are correlated. Results show that both organic matter amounts and fine fractions (clay and silt) were the master factors controlling the bioavailable portion in all soil types.

Introduction

Nowadays a big consideration was given to the pollution of potentially toxic metals and their adverse effects to the ecological system and human health. As a result, lots of studies have been performed to investigate and measuring these constituents as they have the ability to accumulate in the upper layer of soil profile posing environmental risk to the surrounding area (Weber and Karczewska, 2004). Therefore, indicating and measuring the bioavailable amount is very important because it will help for better understanding and estimating of the risk that heavy metals can pose to living organisms. To this end, different researchers have used different chemical reagent to extract the bioavailable fraction because a particular reagent which could be suitable to extract a specific pollutant in some area might not be appropriate for the same metals in different location [1]. To predict and simulate the bioavailable fraction of heavy metals in soil and sediment, researchers have used a wide range of extractants including, mineral acids such as 1 N HCl, buffer solutions for example 1 M NH_4OAc, salt solutions for instance 0.1 M $CaCl_2$, and chelation agents such as EDTA, which has been used in this study, and DTPA [2]. According to MAFF [3] and Gleyzes *et al.* [4], using Ethylene Diamine Tetra Acetic Acid (EDTA), which is considered to be bioavailable to plants, in one step extraction would help to extract the exchangeable, soluble and some of metals bound to carbonate and organic matter. In addition, EDTA, according to McGrath and Loveland [5] has also been used in England and Wales to extract the bioavailable fraction of some studied heavy metals in soils.

It would be worth noting that during the daily life of plants, it usually absorbs by its roots from the soil solution all required materials without considering if the absorbed metals are harmful or not, and thus will change the soil contents of different metals [6]. For example, pointed out that metals in soil solution are in equilibrium state with the exchangeable phase which has linked to the surface of grain particles and the fraction absorbed by functional group of organic matter. As a result, plants will contribute to change the physical criteria of the soil surrounding them, and thereby influencing the bioavailability of heavy metals in soils [7]. Consequently, due to disturbance of the equilibrium state, some metals are very likely to be released to soil from other fractions to be available for plants which were not present before [8]. In addition, the natural processes such as weathering could change the form of metals in the soil and thus affect their mobility and bioavailability in soils. Moreover, there are many factors, such as pH, Eh, organic matter and clay mineral contents, and grain size, that play a significant role in changing the chemical form of heavy metal in soil, and thereby changing their bioavailability capacity in soil [6]. Inka [9],

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